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A FOUNDATION COURSE IN  
CHEMISTRY

FOR STUDENTS OF AGRICULTURE AND  
TECHNOLOGY

J. W. DODGSON  
AND  
J. ALAN MURRAY

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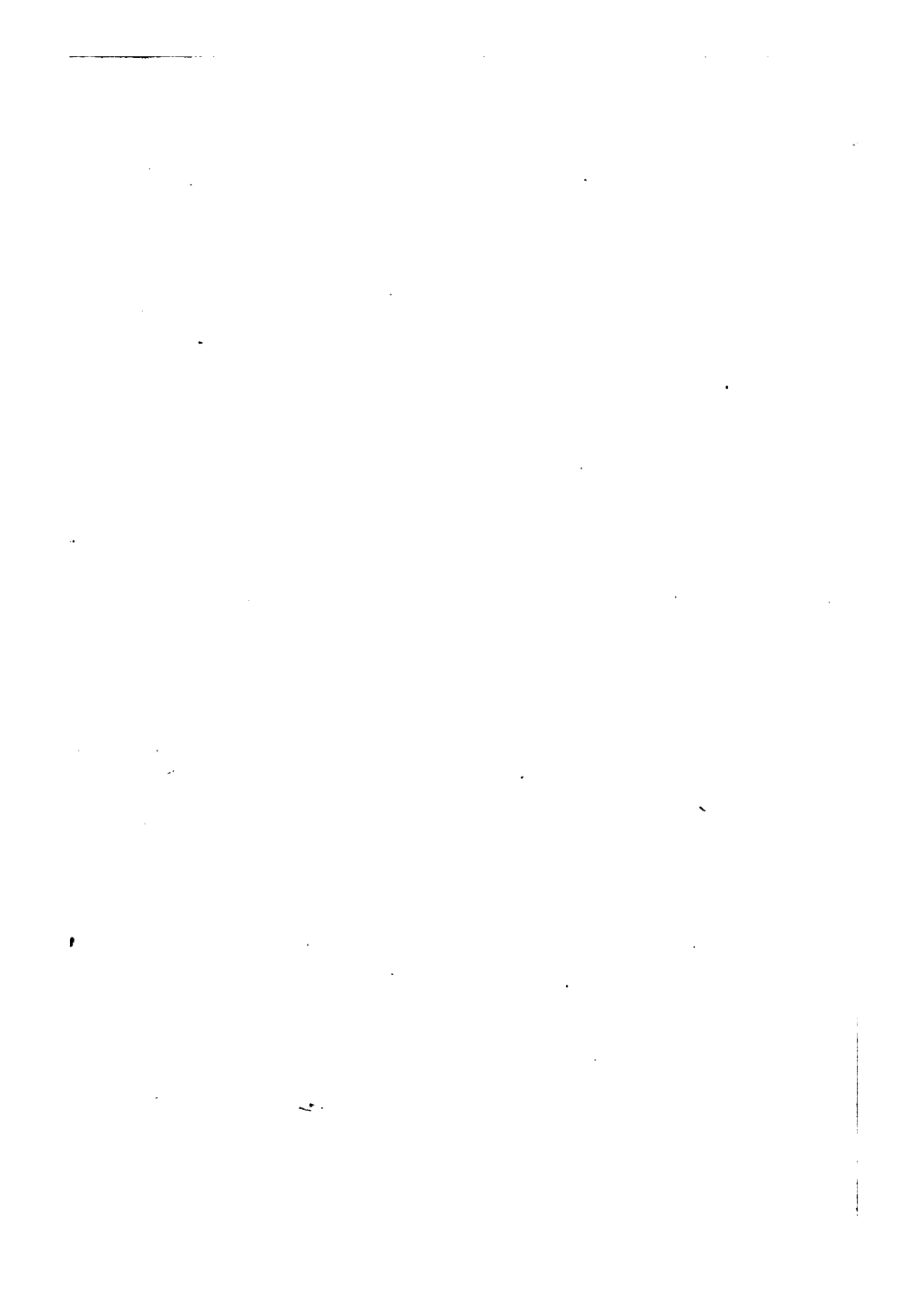


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# A FOUNDATION COURSE IN CHEMISTRY

FOR STUDENTS OF AGRICULTURE AND  
TECHNOLOGY

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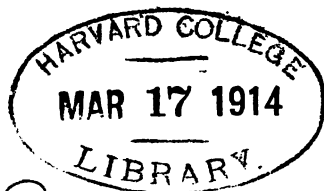
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## PREFACE

THE scope and purpose of this book are indicated in the title. It is intended to give the student such assistance as can be obtained from books in acquiring a knowledge of those fundamental facts and general principles of chemistry upon which the superstructure of agricultural chemistry or other technical application must necessarily rest. Though many excellent works on chemistry have been published in recent years, few, if any, have been expressly designed to meet, or are exactly suited to, the requirements of this large and increasing class of students.

In the present volume the authors have attempted to emphasise those aspects of the subject which are of special importance to such students, while others have been treated in sufficient detail to enable the general principles to be securely grasped. In order to avoid the mischievous tabulation of disconnected facts, matters of purely technical interest have been as far as possible omitted from the text; but numerous footnotes have been added, pointing out the application of the general principles to commercial and industrial processes. These notes should add to the interest of the work and, to a certain extent, give point to the students' reading.

The arrangement of the matter is perhaps somewhat unconventional. The underlying idea is to take advantage of that which the student already knows regarding the common things of life, the things with which every one is more or less familiar, to formulate this knowledge, extend it, and



incorporate the whole in a homogeneous system. The plan is based upon courses of lectures given by the authors during a period extending over many years. They believe it to be theoretically sound; and in practice it has proved efficacious.

The phraseology employed is the simplest that could be used consistently with accuracy and clearness, and all technical terms are fully explained. It is hoped that the book will prove useful to students attending "short courses" in agriculture, horticulture and dairying, as well as to those preparing for College and other diplomas, in these subjects, e.g. the N.D.A., N.D.D., also to those who are attending education courses in hygiene and domestic economy, and in fact to all who take up the study of chemistry as a preliminary to some technical or commercial pursuit.

At the end of the book is placed a selection of questions and problems. These of course are not exhaustive, but are intended to fix the attention of the student upon those portions of his work which are of fundamental importance.

READING

*December, 1912*

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# A FOUNDATION COURSE IN CHEMISTRY

FOR STUDENTS OF AGRICULTURE AND  
TECHNOLOGY

## CHAPTER I

### MATTER AND ENERGY

THE systematic study of the physical universe which we call "Natural Science" deals with two things, "Matter" and "Energy."

**Matter.**—Matter may be defined with sufficient accuracy for our requirements as that which occupies space. It comprises everything which can be touched, handled, weighed, or seen—all things around us, our own bodies included, and of the existence of which we become aware by means of our senses.

Each kind of matter has certain properties of its own which distinguish it from other kinds of matter. Some substances under ordinary conditions are liquid, others gaseous, many solid. Some melt easily, others can only with difficulty be made liquid. Some give off odours, others affect our sense of taste; and it is by recognition of these properties, or of differences in colour, texture, density, etc., that we generally distinguish one kind of matter from another.

**Energy.**—The idea of *Energy*, or the power of doing

mechanical work, is, perhaps, not quite so familiar.<sup>1</sup> Matter and Energy are, however, equally real, so real in fact that we are continually purchasing both. We buy iron, bricks, or other building material. We also buy coal; but we only need that substance that we may burn it, and so liberate the form of energy which we know as heat, and with which we may cause work to be done. We could dispense with the coal if other forms of energy were at our disposal. In districts where there are waterfalls, the energy of the falling water is largely used for doing work which in other places is performed by burning fuel.

Energy differs from matter in that any one form may be changed directly or indirectly into any other form. Thus, in an electric power station, when coal is burnt in the furnaces and heat thereby produced, this form of energy is successively converted into motion of the machinery, energy of the electric current, motion of the tram-cars, and, it may be, light for illumination. Heat, light, sound, motion, are all manifestations of energy.

**Physical Change.**—Matter can exist in three states, solid, liquid, and gaseous, and many substances may be made to assume each of these states successively, generally by the action of heat. The substance which we know as ice, when heat is applied to it, does not become hot, it merely melts, and this change of state represents the work which the heat has done; the liquid formed is water, and this on further application of heat becomes hot, *i.e.* its temperature is raised. After a while it boils and is converted into steam, the gaseous

<sup>1</sup> Treatises on Mechanics give detailed information in regard to Energy, Force, Work, etc. The following definitions should be kept in mind:—

*Force.*—That which produces, or tends to produce, motion in matter.

*Work.*—A force is said to do work when it moves its point of application. It is measured by the product of the force into the distance through which its point of application is moved.

*Energy.*—The power of doing Mechanical Work. There are two kinds of Energy: Kinetic, due to motion, and Potential, due to "position."

*Mass.*—The quantity of matter in a body (a constant).

*Weight.*—The force with which the earth attracts a body (a quantity which varies at different parts of the earth's surface).

form of water. By the application of heat to ice and water we have caused successive changes of state, but the composition of the substance has remained unaltered, nothing has been taken out and nothing put in. A change of state is a physical change.

- When a piece of vulcanite, such as the handle of a fountain-pen, is rubbed vigorously on woollen material it acquires the property of attracting light bodies—dust particles, small pieces of paper, etc.—and is said to be electrified. When an electric current is passed along a wire coiled round a steel bar, the bar becomes capable of picking up other pieces of steel or iron, and if suspended horizontally always sets with one end pointing towards the south and the other towards the north. It is said to be magnetised. Both of these changes are physical. The composition of the vulcanite has not been altered, and analysis can detect no difference between magnetised and unmagnetised steel. The substances have obviously undergone some modifications in their properties, but these modifications have not been accompanied by any change in composition.

**Chemical Change.**—If we mix some of the yellow fusible solid known as sulphur, with about an equal quantity of fine iron filings, they form together a greenish powder from which the iron can be extracted with a magnet and the sulphur removed by a suitable solvent; but if we place the mixture in a glass test-tube and apply heat so as to melt and boil the sulphur, a very vigorous action takes place. The mixture becomes red hot and continues to glow even when removed from the flame. After the action has finished there is in the test-tube a new substance, a grey-black brittle solid from which the solvent previously used will not extract the sulphur, nor a magnet the iron.

This is a change of composition. Two substances have so acted upon one another as to form a third totally different from either of the others in its properties, but which can be shown to contain them both. This is not a physical but a chemical change, and is called *Combination*.

As another instance of such a change, consider what



happens when quick-lime is used for the purpose of making mortar. Water is first thrown upon the hard lumps of quick-lime, which after a short time commence to swell, and then to break into a fine powder. At the same time a large amount of heat is evolved, volumes of steam are given off, and there is ultimately left a dry powder—if the water used has not been too large in quantity—occupying a larger space than the original quick-lime, differing from it in its properties and weighing considerably more. The quick-lime has combined with the water and formed another substance; this product is known as slaked lime.

It is important to notice the evolution of heat both in the slaking of lime and in the action of iron on sulphur, as this is a very common accompaniment to chemical combination.

Again, take the red powder known as red-lead or minium; when strongly heated it becomes yellow in colour, and a gas which causes a glowing splinter of wood to burst into flame is given off. This change is the reverse of the two previously mentioned. The substance, red-lead, has split into two simpler substances, one gaseous, the other a yellow solid. This is also a chemical change but of the kind known as *decomposition*.

Decomposition also takes place when chalk or limestone is heated very strongly. A gas which will extinguish flame is then given off, and a white solid—quick-lime—is left.

Properties such as hardness, density, malleability, fusibility, elasticity, and capacity for being electrified or magnetised are generally referred to as the physical properties of a body, in distinction from its chemical properties which are manifested by its power of uniting with other bodies, or in any way undergoing change of composition.

The two classes of changes which have been described, and which are known respectively as physical and chemical changes, may be briefly differentiated as follows: chemical changes affect the composition of a body, physical changes do not. The latter involve a change in the energy content only.

Chemistry deals with chemical changes, the means of producing and controlling them, the proportions in which

substances take part in them, and the nature and properties of the products.

Chemical changes are not unfamiliar to us. Burning, rusting, decay, are instances which we see daily; and the phenomena of life and growth also involve chemical changes of a very complex nature. No one, therefore, can be entirely ignorant of chemistry, whether he has studied the subject or not. Recognition of this will materially help to simplify the earlier stages of the study.

**Elements and Compounds.**—Substances which can be decomposed are called compounds. Those which have not been decomposed are called elements. Every pure substance belongs to one of these great groups. Some eighty different elements are known, but only about twenty are of common occurrence, and of the remainder some are very rare.

Iron and sulphur are elements: the substance formed when they are heated together is a compound. Red-lead and chalk are compounds; they can be decomposed into simpler substances. The familiar substances, water, salt, sugar, are also compounds.

It is most important to remember that each compound, although it can be split up into simpler compounds or even into elements, is not two or more substances but *one only*.

Compounds must be clearly distinguished from mixtures.

When iron and sulphur are *mixed* together, each retains its own physical and chemical properties, and can easily be separated from the other. It is not until the mixture is heated that the compound is formed. Previous to heating there were *two* elementary substances, afterwards but *one* compound substance. The components of mixtures can often be separated by taking advantage of their different physical properties. Thus, if sand and sugar are mixed together, the sugar may be separated from the sand by its solubility in water, for sand is insoluble. A magnet could be used to extract the iron from a mixture of iron and copper filings, since copper is not attracted by a magnet. If a mixture of iodine and charcoal were gently heated, the iodine would turn into vapour, and could thus be removed from the charcoal which would remain

## 6 A FOUNDATION COURSE IN CHEMISTRY

unchanged. Separation is not always so easily performed as in the instances just given; in some cases complicated processes are necessary, but the method of procedure always depends upon the fact that each substance retains its own specific properties.

There is another and even more important difference between mixtures and compounds. We may *mix* together two or more substances in any proportions we please, but the amounts which enter into chemical combination are entirely beyond our control. Thus, seven parts by weight of iron unite with four parts by weight of sulphur, and twenty-eight parts by weight of quick-lime with nine of water. If we add more of any one, the excess of that one remains uncombined.

There are other forms of chemical action besides combination and decomposition, *e.g.*, "double decomposition," in which two compounds act upon each other exchanging parts and producing two new compounds; and "rearrangement" of elements in which a compound undergoes change within itself, and forms a new compound containing the same elements as the original compound, and in the same proportion, but combined in a different way. It is unnecessary to give examples at this stage, as many instances will arise later.

## CHAPTER II

### AIR

**Nature and Composition.**—Air is a kind of matter. It occupies space. As no two bodies can, simultaneously, occupy the same space, if a vessel be full of air, and it is required to fill it with liquid, it is necessary to provide some means for the air to escape.

The existence of the air is made plain to us, although we cannot see, smell, or taste it, chiefly by the resistance it offers to the passage of bodies through it. This resistance becomes much more appreciable when the air is in motion (wind).

Air forms a gaseous envelope around the earth. It extends to a height of many miles, gradually decreasing in density and altering in composition. It is impossible to state its extreme limits with any accuracy. This envelope of air is called the atmosphere.<sup>1</sup>

Air can be weighed. A method which gives fairly accurate results is as follows: a flask of about one litre capacity (Fig. 1) is fitted with a perforated rubber stopper through which passes a piece of glass tubing about 3 inches in length. To the end of this is attached a short piece of rubber tubing. A mark, B, is made on the neck of the flask, to indicate the end of the stopper and the volume of the flask determined by measuring the quantity of water required to fill it up to B. About 100 c.c. of water, C, is then placed in the flask, the stopper with its fittings is inserted, and the whole apparatus

<sup>1</sup> Gk. *ἀέρας*, air; *σφαῖρα*, a sphere.

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supported over a bunsen flame. After a while the water boils, and the steam produced fills the flask, completely driving out all the air. While the water is still boiling, the india-rubber tube is tightly closed by a spring clamp, and the bunsen burner immediately removed. The apparatus is allowed to cool to the temperature of the room, and is then weighed. The weight obtained is that of the flask and the water, but without air. The clamp is then opened and air can be heard to rush in. The apparatus is again weighed, and is found to be heavier. The difference in weight is due to the air which has entered. The volume of the remaining water must be deducted from the

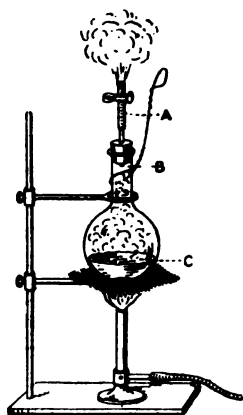


FIG. 1.

whole contents of the flask, in order to ascertain what volume of air caused the increase in weight. From the results obtained, it is easy to calculate the weight of any volume of air. Certain corrections for temperature, pressure, and presence of aqueous vapour have to be made. The general methods of making these corrections are given on page 13. One litre of dry air at 760 mm. pressure and  $0^{\circ}$  C. weighs 1.293 grams.

Air is an excellent example of a gaseous body. Therefore, after having studied some of its properties and discovered its composition, we shall use it for investigating the general properties of gases.

Is air an element, a compound, or a mixture? If we place a piece of phosphorus in a stoppered bell-jar over water, set fire to the phosphorus by touching it with a hot wire and quickly insert the stopper, we shall see dense white fumes given off from the burning phosphorus. When the phosphorus ceases to burn, the white fumes slowly clear away, and as the contents of the jar become cool, the water rises considerably above its original level, showing that part of the air has been removed. The volume of the air which remains is about  $\frac{4}{5}$  of the original,

and it is impossible to burn anything in this residual gas. By burning the phosphorus we have removed that part of the air which supports combustion (p. 16).

If we now add blue litmus (a vegetable colouring matter) to the water it is reddened. The change of colour is characteristic of a class of bodies known as acids (p. 53). It can be shown that the water has acquired this property by the solution of the white fumes.

A modification of the experiment has been used to obtain and examine that part of the air which is removed by burning substances in it. If the liquid metal, mercury, be heated gently for a long time it becomes covered with a red powder; at the same time the air decreases in volume until, as before, about  $\frac{1}{5}$  is removed. If the red powder is separated and heated strongly, it gives off a colourless gas the volume of which is exactly equal to the amount of air removed during the heating of the mercury. If we put a glowing splinter of wood into this gas, the wood bursts into flame.

Air therefore contains two gases, one ( $\frac{1}{5}$  of the total volume) in which a taper burns vigorously, and another ( $\frac{4}{5}$  of the volume) which extinguishes flame. The name given to the first gas is Oxygen (p. 15), the second is known as Nitrogen (p. 21). Neither of these gases has ever been split into simpler substances. They are elements. More exact analyses of air show that the proportions by volume are—nitrogen, 79 per cent.; oxygen, 21 per cent.

Air is neutral to litmus and slightly soluble in water. Like all gases it is more soluble in cold water than in hot, in boiling water it is practically insoluble. If, therefore, water which has been in contact with air for some time is boiled, the dissolved gas is driven off and may be collected. When this gas is examined it is found to be richer in oxygen than ordinary air. This is strong evidence that in the air there are two substances each retaining its own physical properties.

The same conclusion is arrived at from the behaviour of liquefied air. When this is allowed to evaporate freely, the nitrogen boils away first, leaving a liquid very rich in oxygen.

Air is, therefore, not a compound of oxygen and nitrogen,

but a mixture of these elements. An additional proof is obtained by mixing oxygen and nitrogen in the proportions in which they are present in air; there are no signs of chemical action, such as evolution of heat or change of volume, and the mixture is in every respect similar to air.

There are other substances in air besides oxygen and nitrogen; the most important are water vapour, carbon dioxide, ammonia, and sometimes nitric acid and compounds of sulphur, also dust particles, various kinds of bacteria, and other microscopic organisms. It has been found that the nitrogen separated from air is mixed with several other gases even less active than itself; but these occur in very small quantities and, for the present, may be ignored. The amount of water vapour varies considerably. It is generally greater when the air is warm, so that in summer the air contains more than in winter. Carbon dioxide (p. 68) occurs to the extent of about 4 volumes in 10,000, *i.e.* 0.04 per cent. It must not be looked upon as an impurity. It is an essential constituent of air although the amount is so small, and plants depend upon it for their supply of carbon (p. 151). The remaining gases and other substances are impurities which usually occur in larger amounts in the air of towns.

**The General Properties of Gases.**—(1) Gases respond much more readily to alterations of temperature than liquids or solids, though these as a rule increase in volume when heated, and contract when cooled. The volume of each liquid or solid is altered to a different extent by like changes in temperature, but all gases are affected equally. The nature of the gas has little or no effect, provided it is one which is not easily liquefied.

If a small flask be fitted with a perforated rubber stopper and a long bent glass tube in which a short length of mercury prevents escape of air and acts as an index of the volume of the air, very slight warming—such as that produced by grasping the flask in the hand—will cause the mercury to run along the tube owing to the increase in volume of the gas. The actual relation between the volume of a gas and its temperature, which is, as before stated, the same for all gases, is expressed

in the following formula, generally known as Charles's Law (it was discovered by Charles of Paris in 1787):—

*Every gas expands or contracts  $\frac{1}{273}$  of its volume at  $0^{\circ}$  C. for every increase or decrease of  $1^{\circ}$  C., provided the pressure remains unaltered.*

If the volume is kept constant the law will take the form : The pressure exerted by a gas increases or decreases  $\frac{1}{273}$  of its pressure at  $0^{\circ}$  C. for every increase or decrease of  $1^{\circ}$  C.

It is obvious that if this law held throughout all temperatures the gas would cease to exist at  $-273^{\circ}$  C., or, what comes to the same thing, it would exert no pressure. This of course would not take place as the gas would change its state before that extremely low temperature was reached (it has not been reached, up to the present). This temperature " $-273^{\circ}$  C." is often used as a starting point for the measurement of temperature. It is referred to as the absolute zero of temperature, and temperature reckoned from this point is known as absolute temperature. We find this particularly convenient when dealing with gaseous volumes, for Charles's Law can obviously be expressed in the form :—"The volume of a gas is proportional to its absolute temperature." The absolute temperature is found by adding  $273^{\circ}$  C. to the temperature as shown by an ordinary Centigrade thermometer (p. 13).

(2) An even more simple "law" states the effect of alterations of pressure upon the volume of a gas. It is known as Boyle's Law, or Marriotte's Law, and is generally expressed thus: *The volume of a gas is inversely as the pressure, when the temperature remains unchanged.* This means that if the pressure on a gas be doubled, the volume is halved; if the pressure be trebled, the volume is reduced to one-third, and generally in whatever proportion the pressure is increased the volume is diminished in the same proportion.

(3) Gases allow heat to pass through them without being perceptibly warmed; they are sometimes said to be transparent to heat; the scientific term is "diathermanous" ( $\theta\epsilon\rho\mu\acute{o}\varsigma$ , heat;  $\delta\iota\acute{\alpha}$ , through).



(4) Gases can be liquefied by pressure—aided, if necessary, by reduction in temperature—or sometimes by reduction in temperature alone.

**Measurement of Atmospheric Pressure.**—Air exerts pressure upon everything with which it is in contact. This pressure is generally measured by means of some form of barometer<sup>1</sup> (pressure measurer). This, in its simplest form, is merely a glass tube about a yard in length. When it is filled with mercury and then inverted in a reservoir of the same metal, the mercury does not entirely flow out of the vertical tube; a column about 30 inches, or 760 mm., high remains. The height of this column measures the pressure of the atmosphere. In the case of a tube of 1 square inch section, the mercury when standing at a height of 30 inches would have a volume of 30 cubic inches. Thirty cubic inches of mercury weigh  $14\frac{3}{4}$  pounds Avoirdupois, and this is the amount of the pressure of the atmosphere upon every square inch of surface with which it is in contact.



FIG. 2.

Thirty inches, or 760 mm., is the average height of the barometer at sea level, and the pressure supporting this height of mercury is referred to as a pressure of one atmosphere. At heights above the sea level the average pressure is of course less, while it is perceptibly greater in depths such as mines.

(Note that pressure is measured in units of length; *i.e.* the length of the mercury column which the pressure would support.)

**Measurement of Temperature.**—Temperature is usually measured by means of a thermometer.<sup>2</sup> This consists of a thin glass tube, with a bulb at one end, containing mercury, which expands regularly for equal increments of temperature. Three forms of mercury thermometer are in use in Europe, the

<sup>1</sup> Gk. *βάρος*, heavy. Cp. Baryta, Barium.

<sup>2</sup> Gk. *θερμός*, heat; *μέτρον*, a measure. A thermometer, however, does not measure quantities of heat, but differences of temperature.

Fahrenheit, Centigrade or Celsius, and the Réaumur, but they differ only in the graduation of the scale. On all three the same two fixed points are taken, viz. the position of the mercury when the thermometer is placed in melting ice, and its position when in the steam of boiling water. The first is known as the freezing point, the second as the boiling point of water. The difference between the graduations of the three thermometers is shown in Fig. 3.<sup>1</sup>

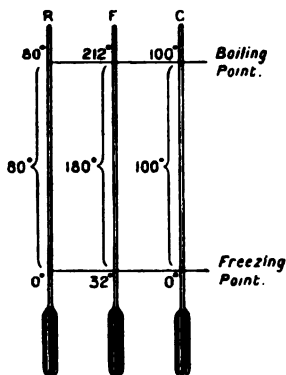


FIG. 3.

#### Corrections of Gaseous Volume for Temperature and Pressure.—

Gaseous volumes are always compared with one another at a pressure of 760 mm. and at a temperature of 0° C. These are known as normal temperature and pressure,<sup>2</sup> but as gases can seldom or ever be measured under exactly these conditions, calculations for finding the volume of the gas at N.T.P. have to be undertaken. An example is here given: 150 c.c. of dry gas are measured at 15° C. and 740 mm. pressure; what volume will the gas occupy at N.T.P.?

- (a) The volume of the gas is proportionate to the absolute temperature and 15° C. is  $15 + 273 = 288^{\circ}$  C. absolute, and 0° C. is  $273^{\circ}$  C. ab. It will measure less at  $273^{\circ}$  than at  $288^{\circ}$ ; we therefore multiply by 273 and divide by 288.

$$\frac{150 \times 273}{288} \text{ c.c. (corrected for temperature).}$$

- (b) The volume of the gas is inversely proportionate to the

<sup>1</sup> To convert degrees on one thermometer into their equivalent on another the following formulae, the explanation of which will be obvious, can be used—

$$F. = \frac{9}{5} C. + 32 \qquad F. = \frac{9}{5} R. + 32 \qquad C. = \frac{5}{9} R.$$

<sup>2</sup> The abbreviation N.T.P. is often used for these words.

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pressure. It will therefore measure less at 760 mm. than at 740; we therefore multiply by 740 and divide by 760.

$$\frac{150 \times 273 \times 740}{288 \times 760} \text{ c.c. (corrected for temperature and pressure).}$$

If the gas be saturated with water vapour, the pressure exerted by the latter must be subtracted from the total gaseous pressure, before the corrections are made.

## CHAPTER III

### THE CHIEF GASES OF THE ATMOSPHERE

**Oxygen.**<sup>1</sup>—Oxygen is the most plentiful element in nature. We have seen that it occurs in air to the extent of 21 per cent.; in the next chapter we shall see that it is also one of the constituents of water. In addition to this, it occurs combined with other elements in most rocks and in the tissues of plants and animals.

The gas was prepared in the year 1774 by Priestley, a chemist, living in Birmingham; and at about the same time by Scheele, a Swedish chemist. They each prepared it by heating the substance then known to chemists as "red precipitate" or "*mercurius calcinatus per se*"; which we have already met with as the red powder formed on mercury when it is gently heated in air for a long time. This substance, on being strongly heated, decomposes into mercury and oxygen, and the gas may be collected in suitable jars, over water.

It is a colourless, odourless gas, very slightly soluble in water, and neutral to litmus. It is a little heavier than air (1 litre weighs 1.43 grams), its density compared with hydrogen<sup>2</sup> is 16 (p. 34). Its general chemical properties are such as to make it, to us, perhaps the most important of all the elements.

<sup>1</sup> Gk. *δξύς*, sour; *γεννώ*, I produce. The name was given to the gas by Lavoisier on the incorrect assumption that it was the essential constituent of acids. The name "Fire Air" which was also given to the gas would have been much more descriptive of its properties.

<sup>2</sup> Hydrogen is the lightest gas known, and is therefore taken as the standard with which other gases are compared as regards density.

If we put a glowing splinter of wood into a jar of oxygen, the splinter immediately bursts into flame and burns vigorously. The same increased energy of combustion is seen when other burning substances are placed in the gas. If, for instance, a piece of sulphur, which burns in air with a dark blue flame, be put, after being lighted, into a jar of oxygen, the flame increases considerably in size, becomes brightly luminous, and of a pale blue colour. Phosphorus burns in oxygen with dazzling brightness; and charcoal, which in air only glows feebly, burns in oxygen with much greater rapidity and brilliancy. Many substances which will not burn in air will burn brightly in oxygen. Perhaps the most striking effect is obtained with iron. If a piece of watch spring tipped with burning sulphur be put into a jar of oxygen, the iron burns rapidly, throwing off brilliant sparks.

The chemical change in all these cases is "Combination." The sulphur, phosphorus, carbon, or iron, combines with the oxygen to form a compound known as an oxide. The oxides of sulphur and carbon are gaseous, the oxide of phosphorus is the white compound mentioned on page 99, the oxide of iron is a brown solid. Much heat is given out when these combinations with oxygen take place, and the burning substance itself, or the products of the reaction, often become white hot or incandescent. The phenomenon is called "Combustion." Ordinary combustion consists in combination with oxygen accompanied by the evolution of light and heat, and for this reason oxygen is often referred to as the supporter of combustion. The relation of the air to combustion is shown in the experiments described on pages 8 and 9, particularly that on page 9, where the oxygen gas is obtained separately. It is the presence of oxygen in the air which allows combustion to take place.

The term "supporter of combustion" requires examination. In the case of a flame at an ordinary gas-burner, we should refer to the coal gas as the combustible body, and the air around it as the supporter of the combustion. But if a lamp chimney be fitted, as shown in the illustration (Fig. 4), in which A is a short, wide, brass or glass tube, B a smaller tube

connected with the gas supply, and C a piece of asbestos board, perforated with a small hole, and the lamp be first filled with coal gas, and the hole in the cardboard closed until the gas comes out from the tube A. If then a light be applied to the issuing gas, on opening the hole in the cardboard, the flame will be drawn up the tube A and will be seen, inside the lamp chimney, surrounded by the coal gas. In this case we should be justified in saying that the oxygen of the air was the combustible body, and the coal gas the supporter of combustion. In truth, the term is applicable to either, but it is generally applied to that gas which surrounds the flame, and in all ordinary circumstances this is air, or oxygen.<sup>1</sup> If we lived in an atmosphere of coal gas we might be burning oxygen at gas-jets.

The rusting of iron is an example of very slow combination with oxygen. If some clean iron filings, moistened with water, be suspended in a muslin bag, in a jar of air standing over water, and allowed to remain for several days, the iron becomes very "rusty," and the water rises just as if phosphorus had been burnt in the jar, and to the same height. Iron, therefore, when moistened, removes oxygen from the air, forming iron rust, which is oxide of iron combined with water.

The amount of heat given out on combination with oxygen is different for each substance, but for any given kind of material it is proportional to the mass of the substance which enters into combination. Thus, when 1 gram of carbon is burned completely 96,960 units<sup>2</sup> of heat are evolved. One

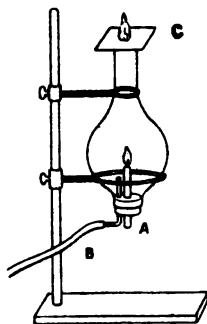


FIG. 4.

<sup>1</sup> We have referred to oxygen as "*the* supporter" not "*a* supporter" of combustion. As ordinary combustion consists in combination with oxygen, oxygen is the only possible supporter of combustion of this type. Other kinds of combustion will be referred to when treating of the chemistry of other elements.

<sup>2</sup> A unit of heat is the amount of heat required to raise 1 gram of water through 1° C.

gram of hydrogen on burning causes the evolution of 68,360 units of heat. If combination takes place rapidly, the heat is given out rapidly, and the substances get very hot; but if the combination takes place slowly, the heat is evolved slowly, and the temperature is not appreciably raised. Although the two actions are absolutely identical, the difference between the temperature produced by iron rapidly burning in oxygen and slowly rusting in air is an instance of the effect of increasing the rapidity of the chemical action. A more familiar example is seen in the effect of forcing air through a fire by means of bellows, and so giving the fire a continual supply of fresh oxygen. The fire burns more rapidly and becomes much hotter, as the heat given out by the burning coal is evolved in a shorter time. In general, the faster anything burns the higher the temperature produced. Nearly all elements combine with oxygen; although several will not do so directly, they can be made to combine by various indirect methods.

When substances combine with oxygen slowly (e.g. the rusting of iron) they are sometimes said to undergo slow combustion. Heat is given out, but not with sufficient rapidity to cause incandescence or flame. The respiration of animals may be looked upon as an instance of slow combustion, and this statement shows why oxygen is necessary for the support of animal life. The effect upon animals of removing the oxygen from the air is to cause suffocation and death, while increase in the percentage of oxygen leads to increased activity within certain limits. Animals, however, could not long continue to breathe pure oxygen; it would act as a poison, producing intense inflammation, convulsions, and death.

Although oxygen occurs free in the atmosphere, its separation in a pure state presents considerable difficulties. It is therefore generally prepared in the laboratory from certain of its compounds. Some of the oxides are suitable for the purpose. Manganese dioxide is sometimes used. This substance, when strongly heated, loses a portion of its oxygen. Red-lead (p. 209) and oxide of mercury (p. 210) have already been shown to behave in a similar manner, but none of these provide a perfectly satisfactory method of preparation, for

the amount of oxygen evolved is small in comparison with the weight of oxide used, and in the case of mercury oxide the substance itself is somewhat expensive.

The material most generally employed is potassium chlorate, a compound of oxygen with the elements chlorine and potassium. This compound, on being heated strongly, loses all its oxygen, and leaves a residue consisting of potassium combined with chlorine only. Admixture with certain other substances causes potassium chlorate to part with its oxygen at a lower temperature; manganese dioxide is most often used, but a still more powerful effect is produced by iron oxide, and even powdered glass or sand facilitate the liberation of the gas. In all cases only the potassium chlorate undergoes decomposition.

The apparatus employed for the preparation of small quantities of oxygen is shown in the illustration (Fig. 5).

Oxygen is an article of commerce and is used largely both for medical purposes and in various industries. It is supplied under great pressure in wrought-iron cylinders.

The usual commercial method for preparing oxygen is a process of obtaining it indirectly from the air.

When barium oxide, a substance very like quick-lime, is heated in air or oxygen to a temperature not exceeding  $550^{\circ}\text{C}$ . it combines with additional oxygen forming barium peroxide. This is decomposed again into barium oxide and oxygen when more strongly heated. By alternately heating and cooling barium peroxide a continual supply of oxygen may be obtained, without any decrease in the amount of barium oxide. This is obviously an economical method, but as it is inconvenient and expensive to continually raise and lower the temperature, the barium compound is kept at a constant high temperature and the pressure varied by means of air pumps.

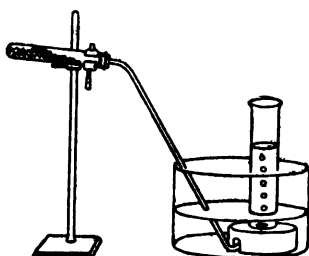


FIG. 5.



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When the pressure is high the substance takes up oxygen from the air, and when the pressure is reduced the oxygen is again evolved and may be collected.

Another method of obtaining oxygen from the air promises to become of commercial importance. Air liquefied by intense cold and great pressure is allowed to evaporate freely at ordinary atmospheric pressure. Under these conditions the nitrogen boils away first, leaving a liquid which may contain as much as 95 per cent. of oxygen. The temperature at which this evaporation takes place is of course very low, for nitrogen boils at  $-194^{\circ}\text{C}.$ , while the boiling point of oxygen is  $-182.5^{\circ}\text{C}.$  The gas obtained by evaporation of the residual liquid is pumped into cylinders and sold as compressed oxygen.

Liquid oxygen is pale blue in colour. Gaseous oxygen is soluble in water to the extent of about 4 volumes of the gas in 100 of water at  $0^{\circ}\text{C}.$  Fish derive the oxygen they need from this source, their gills being the respiratory organs by which they make use of the dissolved gas.<sup>1</sup>

By passing an electric spark through oxygen, or by submitting it to the silent electric discharge, oxygen is caused to undergo contraction in volume, and a modified form of the gas is produced which is known as ozone (p. 92).

<sup>1</sup> Despite the fact that respiration and combustion are both processes of oxidation, they stand in a somewhat different relation to the amount of oxygen in the air. In the case of the former, it is the actual quantity of oxygen that is important; in the latter it is the percentage. When the amount of oxygen in air is reduced, animals unconsciously breathe more deeply and so take in more oxygen. Human beings experience no inconvenience even when one-third of the oxygen normally present in the air is removed, *i.e.* when it is reduced to 14 per cent. But if the amount of oxygen be reduced to 10 per cent. (less than half), the air will not properly support respiration and persons breathing it experience some of the sensations of suffocation.

Burning substances differ widely from one another in their sensitiveness to deficiency of oxygen; thus the flame of marsh gas (p. 139) is extinguished when the amount of oxygen in the air is reduced to  $17\frac{1}{2}$  per cent., and that of a candle when the oxygen is reduced to 17 per cent. Hydrogen continues to burn till only  $7\frac{1}{2}$  per cent. of oxygen is left, and phosphorus, till practically all the oxygen is removed. It will be seen, therefore, that the popular notion that air which extinguishes a candle flame is not capable of supporting respiration is not based on fact; such air may or may not be fit to breathe.

**Nitrogen.**—The facts we have already discovered in connection with the gas are: it is colourless, tasteless, odourless, neutral to litmus, less soluble in water than oxygen, and chemically very inactive. In fact it exhibits less tendency to unite with other elements than any other of the common gases. Its most important properties are therefore of a negative character. It is obviously not poisonous, and in the air its chief function is to dilute the oxygen. A few substances, such as magnesium and potassium, combine with nitrogen when heated strongly, and at the temperature of the electric spark the gas combines with oxygen, a fact of great importance in agriculture (p. 132). A certain amount of combination of these gases takes place during thunderstorms.

It has already been shown that nitrogen can be obtained from the air by burning phosphorus (p. 8) in it. A better method is to pass the air over heated copper; this forms copper oxide and leaves the nitrogen, which can be collected over water. Burning a candle in air would not be effective, for not only would the nitrogen left be mixed with the products of combustion (carbon dioxide and water vapour) but the candle would be extinguished long before all the oxygen was removed from the air.

These can scarcely be regarded as methods of preparing nitrogen; they are, rather, ways of removing the oxygen with which it is mixed, and, moreover, the nitrogen thus obtained still contains other inactive gases, the presence of which causes it to be slightly heavier than the pure gas.

Nitrogen is most easily prepared in a pure state from ammonium nitrite, which, on heating, decomposes entirely into nitrogen and water. It is convenient to use a mixture of sodium nitrite and ammonium chloride dissolved in water. The gas is collected over water.

Nitrogen is an essential constituent of the tissues (fats and certain others excepted) which form the bodies of plants and animals, and is necessary for their growth. No animals, and very few plants, however, can utilise free nitrogen. Plants in general require that it should be supplied in the form of comparatively simple compounds; animals obtain their nitrogen

from foods, *e.g.* flesh, casein, gluten, etc.,<sup>1</sup> which are compounds of a much more complex nature.

Some plants, such as the leguminosæ, apparently take up atmospheric nitrogen. This is effected by means of certain bacteria which, being present in the soil, enter the root hairs and grow inside the cortex producing small tubercles. These bacteria assimilate nitrogen directly from the air and convert it into compounds which the plant is able to utilise.

<sup>1</sup> Some plants, *Dionæa* (Venus' fly-trap), *Drosera* (sun dew), the various forms of pitcher plant (*Nepenthes*), have the power of assimilating nitrogen from highly complex compounds such as those which form the bodies of insects.

## CHAPTER IV

### WATER

No substance is more familiar than water. It exists in such immense quantities that it covers by far the greater part of the earth's surface. Although it is so common, it is difficult to obtain in a perfectly pure condition, owing to the fact that it dissolves, to a greater or less extent, such a large number of substances, solid, liquid, or gaseous. Natural waters invariably

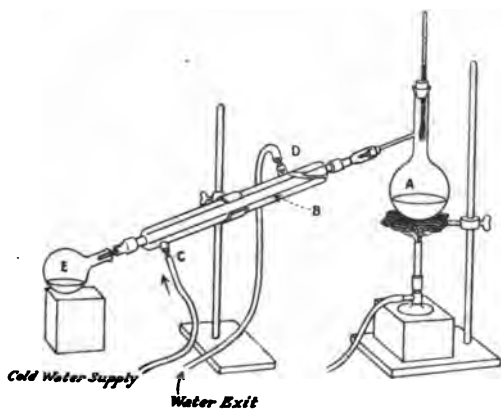


FIG. 6.

contain such substances in solution. Water also often contains solid particles which have not dissolved, but remain suspended in the liquid. They can be separated by filtration. The filter used in laboratories is generally a circular piece of purified paper, folded in four, opened so as to form a cone and fitted

into a funnel. Substances in solution cannot be removed by filtration; in order to effect this the liquid must be distilled.

A form of apparatus in common use is shown in the diagram (Fig. 6). A is a flask containing the water to be distilled; it has a side tube in the neck, and is fitted with a cork through which a thermometer is passed. The water in A is boiled, and the steam passes by the side tube through the condenser B. This consists of a straight tube surrounded by a jacket of cold water which enters at C and leaves the condenser at D. The condensed steam is collected in the flask E. The distilled water thus obtained is free from solids in solution, and if the first portion of the distillate is rejected, it is also free from dissolved gases.

The temperature at which water boils at ordinary pressure is, as has already been shown, one of the fixed points on the thermometer, and is marked on the Centigrade scale as  $100^{\circ}$ . The boiling point is, however, dependent upon the atmospheric pressure. The higher the pressure, the higher the temperature to which the water must be raised before it boils. If the pressure be low enough water can be made to boil when it is almost cold. The apparatus described on page 8 (Fig. 1) may be used to illustrate this.

Boil the water and close the indiarubber tube, as described, and then hold the flask under the tap and pour cold water upon it. The water which ceased boiling when the flame was removed, will again begin to boil, and can, by continuous cooling, be made to do so until the flask scarcely seems warm to the hand. For this experiment to be successful, it is essential that all the air should have been driven out of the flask, for the water boils at the lower temperature because the rapid cooling condenses the steam and thereby lowers the pressure inside the flask.

Pure water is, at ordinary temperatures, a tasteless, odourless liquid, colourless when viewed in small quantity, but pale greenish blue when seen in considerable thickness. It has no effect upon the colour of litmus; that is, it is neither acid nor alkaline (pp. 53, 54).

**Physical Properties of Water.**—It is a very feeble conductor of heat. This can be demonstrated by heating a test-tube full of water near the top ; the water in the upper portion will boil, while that at the bottom remains quite cold. In order, therefore, to raise the temperature of large quantities of water, it is necessary to apply heat from below. Like most other substances, water expands when heated and so becomes less dense. When, therefore, a vessel of water is placed over a flame, the water nearest the flame gets heated first, and becoming less dense, rises through the cooler and heavier liquid which streams down to take its place. A system of currents, known as *convection* currents, is thus set up which gradually distributes the heated water through the whole mass, until it has all been heated to the boiling point.

This method of heating does not apply to water only, but to most liquids and gases ; air, for example, is warmed by contact with the heated surface of the ground, and it is partly by this means that the air currents known as winds are produced.

If instead of heating the water we cool it, it will contract in volume and become denser until the temperature of  $4^{\circ}$  C. ( $39.4^{\circ}$  Fahr.) is reached, when, unlike other liquids, it will on further cooling begin to expand, and the expansion will continue until the freezing point is reached. At the moment of the change in state there is a great increase in volume, so that ice is considerably lighter than water, and floats upon it ; its density as compared with water is 0.91. The expansion of water on being cooled below  $4^{\circ}$  C. explains why ice is formed on the surface of lakes and not at the bottom, while the expansion on freezing is the cause of the ice being pushed up the banks ; it accounts also for the bursting of water-pipes during hard frost. Of course, the breaking of the pipe is not generally noticed until the thaw comes when the water from the melting ice escapes. Rocks are also split by the freezing of water in their crevices, and soils are pulverized.

The presence of substances in solution lowers the freezing point and raises the boiling point of water (p. 116).

When heat is applied to ice it melts. If a thermometer is

placed in melting ice and the mass is kept stirred, the thermometer will indicate no rise in temperature as long as any ice remains unmelted. The heat has been used entirely in causing change of state. The amount of heat necessary to melt a substance is usually referred to as the latent heat of the liquid. Thus, in the case of ice, the heat necessary to turn it into water is called the latent heat of water. Similarly, the heat required to change water into steam is called the latent heat of steam. The quantities of heat requisite to bring about these changes of state are large; the heat used in melting 1 gram of ice is sufficient to raise the temperature of 80 grams of water through  $1^{\circ}\text{C}$ ., *i.e.* 80 units of heat,<sup>1</sup> while as much as 537 units of heat are required to vaporise 1 gram of water.

When water is heated, its temperature rises very slowly. If, for example, equal masses of mercury and water were separately caused to receive heat at equal rates, the mercury would get hot much more rapidly than the water, and the same statement applies in varying degrees to all other substances. In other words, water takes more heat to make it hot than does any other substance. It is said to have a larger capacity for heat (thermal capacity) or to have a high specific heat.<sup>2</sup> This property of water is of great importance, for substances which when heated get hot slowly also cool slowly. It is for this reason that hot water and steam are used for warming houses; and absence of extremes of summer heat and winter cold in insular climates is due to the moderating effect of the water of the ocean.

**Solutions.**—Water is a very general solvent. It dissolves most substances to an appreciable extent, but the permanent tissues of plants and animals, indiarubber, resins, and some

<sup>1</sup> P. 17, note (2).

<sup>2</sup> These two terms do not mean exactly the same thing. The *thermal capacity* of a substance is the number of units of heat required to raise 1 gram of the substance through  $1^{\circ}\text{C}$ entigrade, and is therefore a quantity of heat. The *specific heat* is the ratio—

$$\frac{\text{Heat required to raise a given mass of the substance through } 1^{\circ}\text{C.}}{\text{Heat required to raise the same mass of a standard substance through } 1^{\circ}\text{C.}}$$

and water is always taken as the standard substance.

others are practically insoluble. Soluble substances, moreover, differ greatly in their degree of solubility, and for each substance the amount that will dissolve depends upon the temperature

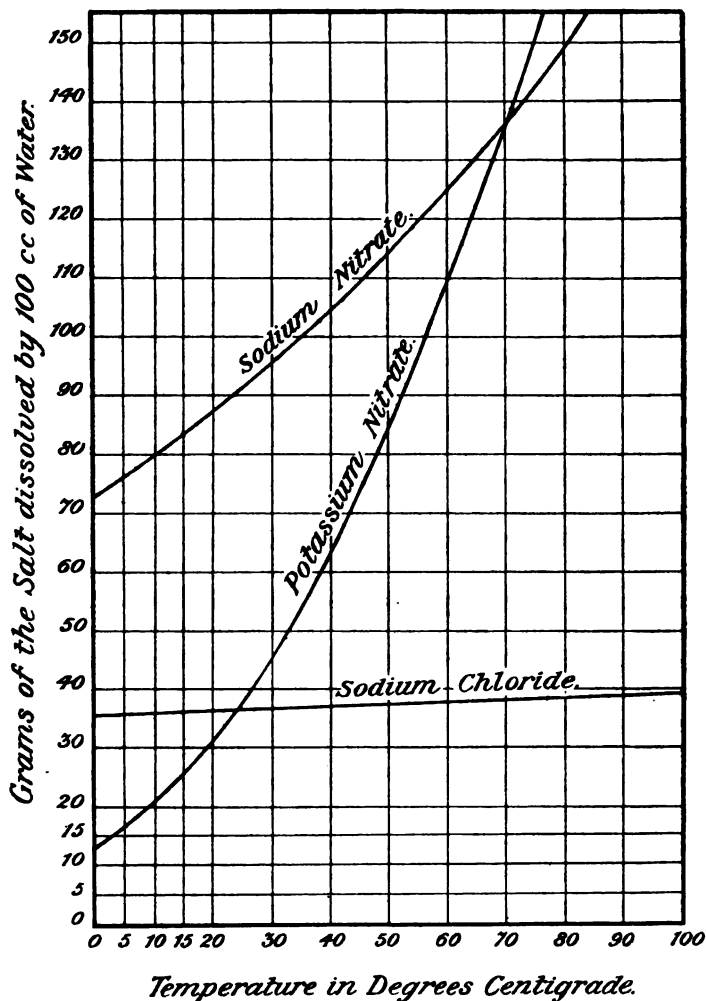


FIG. 7.—SOLUBILITY CURVES.



of the water. Generally, a rise of temperature causes the water to dissolve a larger quantity of the solid. In some cases this is very marked. Chloride of lead dissolves in hot water with comparative ease, while its solubility in cold water is very small. On the other hand, common salt is nearly as soluble in cold water as in hot. It is customary to represent graphically, in the form known as a "Solubility Curve," the relation between temperature and the quantity which enters into solution. Fig. 7 is a series of curves for certain well-known substances. The temperature is marked on the bottom horizontal line, the vertical measurements give the number of grams of the substance in 100 c.c. of the saturated solution.

Liquids which are soluble in water are generally said to be miscible with water. Alcohol is miscible with water in all proportions, and so is sulphuric acid; but other liquids, such as ether, chloroform, and oils, are either insoluble or only dissolve to a slight extent. When shaken with water and allowed to stand they separate, the lighter liquid forming the upper layer. In the case of ether this upper layer would be ether mixed with a little water, while the lower layer would be water mixed with a small quantity of ether.

The solubility of gases in water depends not only upon temperature but also upon pressure. As a general rule, increase of temperature rapidly diminishes the solubility of gases in water, so that it is often possible to expel all the gas from solution by boiling, hydrochloric acid (p. 78) is an important exception. Increase of pressure increases the solubility of gases. Carbon dioxide, for example, is not very soluble in water, but in the manufacture of aerated waters it is forced into water under great pressure and remains dissolved. When the cork is removed from the bottle the gas escapes with brisk effervescence because the pressure is reduced.

**Crystallisation.**—When water at any temperature has dissolved as much of a solid as it is capable of doing, the solution is said to be saturated. If the temperature of the saturated solution be raised it is generally no longer saturated, but will take up a further quantity of the solid. If the temperature of the saturated solution be lowered part of the solid will separate

until only sufficient remains dissolved to saturate the solution at the lower temperature. The solid generally separates in the crystalline form. The crystals of each kind of substance have a characteristic shape. They have flat surfaces<sup>1</sup> and straight edges, but they are of many different forms. Crystals may also be formed by allowing the solution to evaporate. If a solution is saturated when a certain quantity of water is present, some of the solid must separate when part of the water is removed. The more slowly evaporation takes place the larger are the crystals formed.

In many cases crystals which are apparently quite dry contain water. Such water is known as water of crystallisation.<sup>2</sup> When this water is removed, the substance loses its crystalline form. Occasionally crystals lose water on exposure to the air and become covered with a powder; they are said to "effloresce." Some substances take water from moist air and dissolve in it; they are said to be deliquescent.

In many cases the presence of water of crystallisation alters the colour of a substance. Thus, copper sulphate, which, when anhydrous (*i.e.* without water) is yellowish white, forms blue hydrated crystals; and the salts of cobalt are generally pink when they contain water, but are blue when anhydrous.

**Natural Waters.**—Natural waters always contain many impurities in solution. Rain-water—particularly that which falls in country districts after a previous rainy period—is the purest, but even this contains foreign matter washed out of the atmosphere. Sea-water has common salt and other substances dissolved in it. Water from rivers, lakes, and springs contains impurities, generally harmless. The nature of these depends upon the nature of the rocks with which the water has been in contact. The waters of some springs contain considerable quantities of mineral matter in solution, *e.g.* salts of iron, calcium, magnesium, potassium, and sodium, and compounds of sulphur. Such springs are often known as mineral springs. In some cases the water is so highly charged with carbon dioxide as to

<sup>1</sup> There are substances which occasionally occur as crystals with curved faces. The diamond is the most important example.

<sup>2</sup> Water of hydration is perhaps a better term.

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be strongly effervescent. Water containing large quantities of the salts of calcium or magnesium is said to be hard (p. 69). Water used for domestic purposes should be examined, not only to ascertain the degree of "hardness," but also with special reference to the organic matter it may hold in solution. This organic matter is often present owing to admixture with sewage. The organic matter itself may be harmless, but the bacteria of putrefaction and disease which may come with it are extremely dangerous.

#### ANALYSES OF TYPICAL NATURAL WATERS

PARTS PER 100,000

	Free ammonia.	Albuminoid ammonia.	Chlorine.	Total solids.	Hardness.		Nitrogen as nitrates and nitrites.
					Temporary.	Permanent.	
Rain water . .	0'024	0'015	0'22	2'95	—	—	0'003
Upland surface water . . .	0'002	0'032	1'13	9'67	1'5	4'3	0'009
Deep well water	0'010	0'018	5'11	43'78	15'8	9'2	0'495
Spring water .	0'001	0'013	2'49	28'20	11'0	7'5	0'383
Sea water . .	0'005	0'165	1975'6	3898'7	48'9	748'0	0'033
Shallow well .	0'091	0'126	5'7	18'5	2'0	1'4	0'000
River water .	0'001	0'059	1'75	11'16	—	6'0	0'081

In order to form an opinion of the purity of a sample of water, the results of analysis should be considered as a whole and in relation to one another. No definite rules can be laid down, but the following general directions should be kept in mind.

Contamination with animal matter—sewage, etc.—increases the amount of nitrogen, especially that present as free ammonia, and of chlorine. Vegetable matter also increases the amount of nitrogen but not of chlorine, and in this case the amount of albuminoid ammonia will generally be much greater than that of the free ammonia. Chlorine may be derived from mineral sources, but in that case the amounts of free and albuminoid ammonia will both be low.

Very hard waters are unsuitable for many domestic purposes, and it is said that they are liable to cause inflammation in young children and invalids ; but they are not harmful to healthy adults.

Analysis of several waters are given in the table above. On studying the figures and bearing in mind these directions, it will be obvious that in these particular specimens the shallow well

water is polluted with animal matter and the river water contains some vegetable matter. The other drinking waters are apparently free from organic contamination.

**The Composition of Water.**—Pure water does not conduct the electric current. If a small quantity of a mineral acid, such as sulphuric acid, be added to the water then the current will pass through it, but the water is decomposed (p. 4).

This method of decomposition is known as electrolysis; it is conveniently performed in an apparatus of the form shown in the illustration (Fig. 8). The acidulated water is poured into the apparatus by the funnel E until it begins to run out at the taps C and D, which are then closed. An electric current is then passed through the liquid by connecting the platinum plates (electrodes) A and B to the two ends of a battery. Bubbles of gas immediately rise from each electrode and accumulate in the upper part of each of the side tubes. After a short time it will be observed that the gas in one tube is greater in quantity than that in the other—in fact, it will be exactly twice as much—and this proportion will be maintained as long as the gases continue to be evolved. The gas in the tube which contains the smaller amount will cause a glowing splinter of wood to burst into flame. It is oxygen. That in the other tube will burn. It is hydrogen.<sup>1</sup> Water therefore consists of hydrogen and oxygen combined in the proportion of two volumes of hydrogen to one volume of oxygen. It is obvious that water cannot be a mixture of these two gases, as it is totally unlike either of them.

Further proofs of the composition of water are given later (p. 35).

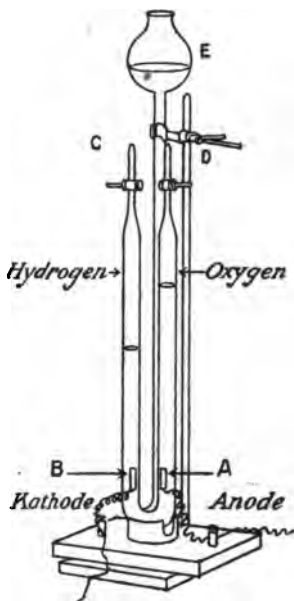


FIG. 8.

<sup>1</sup> Gk. *ῥῆμα*, water.

## CHAPTER V

### HYDROGEN

**Preparation.**—The inflammable gas liberated from water by electrolysis can be obtained more conveniently in other ways, the more important of which may be grouped in two divisions.

A. From water, by the action upon it of various metals.

If a piece of sodium about the size of a small pea be thrown upon the surface of water, the metal, being lighter than water, floats; it melts, showing that heat is developed, and assumes a spherical shape; it rolls about over the water and gradually dissolves. If, however, the sodium be placed upon a floating filter paper, and is thereby prevented from moving, and consequently from being cooled by contact with the colder water, the sodium will apparently burst into flame. This is the flame of hydrogen which the heat of the reaction is now sufficient to ignite. The gas may readily be collected, if the sodium be wrapped in wire gauze and held under the water. A still more convenient method is to dissolve the metal in mercury, forming a paste known as sodium amalgam. The presence of the mercury makes the reaction take place more slowly, so that but little rise in temperature occurs, and its weight causes the amalgam to sink to the bottom of the water.

If potassium be used, it behaves in a similar manner, but more heat is developed, and the liberated hydrogen takes fire even while the metal is rolling over the surface of the water.

The violet colour of the flame is due to the presence of vapour of potassium (p. 96), the yellow colour of the flame in the previous experiment was due to vapours of sodium (p. 80). The decomposition of water is also effected by calcium. In each case the metal combines with the oxygen of the water, forming a compound which dissolves and imparts to the water a "soapy" taste and makes it alkaline. The calcium compound is not very soluble and largely separates as a white solid.

The metals already mentioned decompose water at ordinary temperature. Others do so when the temperature is raised. If metallic magnesium is boiled with water, hydrogen is liberated; the reaction is assisted by the presence of a small quantity of magnesium chloride in the water.

Decomposition of water by magnesium may also be carried out by passing steam over the heated metal.

Iron decomposes water at a red heat. This gives a cheap method of preparing large quantities of hydrogen. Iron filings are placed in an iron tube which is heated to redness in a furnace; and while the filings are red hot, the steam from boiling water is passed over them.

B. From acids by reaction with metals.

Hydrogen is more conveniently prepared by the action of certain metals upon a class of substances known as acids (Chap. VII), all of which contain hydrogen. The most convenient acids to use are hydrochloric acid (spirit of salt) (p. 73) and sulphuric acid (oil of vitriol) (p. 91), and the metals most usually employed are zinc and iron.

Zinc is the more suitable metal, as iron is always very impure, and the hydrogen which is given off when it acts upon acids is mixed with other gases which obscure its properties. The sulphuric acid must be

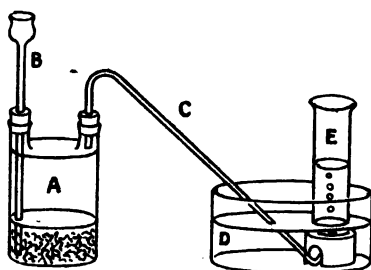


FIG. 9.

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dilute ; if the concentrated acid is used very little action takes place and no hydrogen is evolved (p. 62).

When zinc or iron acts upon acids, the metal dissolves and the resulting compounds may be obtained in a crystalline form on evaporation of the solution (p. 28).

Other metals, such as aluminium and magnesium, as well as those which decompose water at ordinary temperatures, might be used, but they would be either more expensive than zinc or iron, or the reaction would not be so easily controlled.

**The Physical Properties of Hydrogen.**—It is the lightest substance known. It is generally used as the standard of density for gases. By this we mean that we state the density of a gas by saying how many times a given volume of it is heavier than an equal volume of hydrogen under the same conditions of temperature and pressure. A litre of hydrogen weighs 0.0898 gram.

Owing to its extreme lightness it is used for inflating balloons,<sup>1</sup> and the more modern dirigible air-ships.

Hydrogen is less soluble in water than either oxygen or nitrogen ; 100 volumes of water dissolve only about 2 volumes of hydrogen at 15° C.

It is colourless, odourless, and without any action upon litmus. It is not poisonous.

Hydrogen has been liquefied and solidified. Under ordinary atmospheric pressure it boils at about -252° C.

Many metals have the power of absorbing (occluding) hydrogen. Iron, when heated, takes up 19 times its own volume of gas, and finely divided platinum 50 times its own volume.

**The Chemical Properties of Hydrogen.**—It combines readily with oxygen and with chlorine (p. 74). It is a reducing agent, that is, it will take oxygen away from substances which contain that element in a state of combination.

Experimental demonstration :—1. If a jar of hydrogen

<sup>1</sup> Coal gas, density about eight times that of hydrogen, is used for ordinary balloons.

be held mouth downwards and a lighted taper be introduced, the gas takes fire and burns at the mouth of the jar, but the flame of the taper is extinguished. The taper requires oxygen to enable it to burn, while inside the jar there is only hydrogen, with which the material of the taper does not combine.

2. If a jar of hydrogen be held mouth upwards, and a lighted taper applied, the flame of the burning gas will rapidly run down the whole length of the jar, owing to more thorough mixing with air.

3. In a mixture of two volumes of hydrogen with one volume of oxygen the combination is so rapid as to produce violent explosion.

The explosion of hydrogen with oxygen yields a *proof of the composition of water by volume*. If the gases, in the proportion of two volumes of hydrogen to one of oxygen, be mixed in a tube over mercury and exploded by an electric spark, they entirely disappear and a small globule of water is the only product.

4. When dry hydrogen gas is passed over heated copper oxide, it combines with the oxygen, and water and metallic copper are produced.

This experiment enables us to estimate directly the *composition of water by weight*. The water formed during the reaction is collected and weighed, the loss in weight of the copper oxide is the weight of the oxygen present in the water, and the difference between these two weights is the weight of hydrogen used. By this means it can be shown that hydrogen combines with oxygen in the proportion of 1 to 8 by weight. This is the same as 2 to 1 by volume, for oxygen is 16 times as dense as hydrogen.

All substances which contain hydrogen yield water as a product of combustion. This can readily be proved in the case of a candle or gas-flame by holding over it a cold glass vessel, such as a clean dry beaker. The surface of the beaker will be covered immediately with a film of dew. Rooms in which much coal-gas is burnt (coal-gas contains hydrogen) show the presence of water-vapour in the air by a copious



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deposit upon the window-panes, particularly in winter time. Water-vapour in considerable quantities is also present in respired air. The heat evolved during the combustion of hydrogen is often utilised. Most of the substances we use as fuels (petroleum, coal-gas, etc.) contain hydrogen (p. 142).

## CHAPTER VI

### GENERAL PRINCIPLES

**Nomenclature.**—Some of the chemical elements, such as sulphur and iron, have been known from time immemorial, and their colloquial names are often used in chemistry. Languages, however, differ greatly, and in order to obtain a universal notation the Latin names for these elements, when such names exist, are usually employed for the purposes of symbolic notation (p. 39). Elements more recently discovered have in some cases received names descriptive of their more striking and obvious properties. Chlorine,<sup>1</sup> for example, was so called because the gas exhibits a greenish-yellow colour; bromine,<sup>2</sup> because of its objectionable and powerful odour; chromium,<sup>3</sup> because its compounds exhibit a great variety of colouring.

The Latin names for metals generally ended in "um"; so when a substance of this kind was prepared from potash—which is simply potashes (p. 95)—it was called, in English, "potassium."<sup>4</sup> Similarly, the metal obtained from soda was called sodium, and so on.

Some chemical compounds, such as water, salt, etc., have of necessity been known throughout all history, and in every language they are still popularly called by names given them long ago. These names, however, are not generally

<sup>1</sup> Gk. *χλωρός*, greenish yellow. Cp. chlorophyll, literally leaf green. Gk. *φύλλον*, a leaf.

<sup>2</sup> Gk. *βρώμος*, a stink.

<sup>3</sup> Gk. *χρώμα*, colour. Cp. chromatic.

<sup>4</sup> Some of the so-called Latin names are, of course, merely Latinised forms of English words, others are, as shown, Latinised forms of Greek words.

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used in chemistry because they tell us nothing about the substances they refer to. It has been found more convenient to use names which show what the compounds are composed of, and a scientific system has been invented for the purpose.

A compound must contain at least two elements, and the name of the compound is made up from the names of both constituents. Such names therefore generally consist of two words. When the substance is composed of two elements only (a binary compound), one of the words ends in "ide." Thus the chemical name for water is *oxide* of hydrogen, because it is a compound of oxygen and hydrogen; the chemical name for common salt is *chloride* of sodium, because it is a compound of chlorine and sodium. When sulphur and copper combine together, the compound is called *sulphide* of copper. The word "of" is frequently omitted. We may say more shortly, hydrogen oxide, sodium chloride, copper sulphide.

In some cases, two different compounds can be obtained from the same two elements. They are distinguished by the terminations *ous* and *ic*. The element iron forms two compounds with the element chlorine. One of these contains 59.9 per cent. of chlorine; the other contains 65.5 per cent. The former is called *ferrous*<sup>1</sup> chloride, and the latter *ferric*<sup>1</sup> chloride. The universal rule is that the name of the compound which contains a smaller proportion of oxygen, chlorine, sulphur, etc., ends in "ous," and that of the compound which contains the larger ends in "ic."

When there are more than two compounds of the same two elements we resort to the use of prefixes. In the case of nitrogen and oxygen, no less than five different compounds are known. They are called respectively, nitrogen *monoxide*, nitrogen *dioxide*, nitrogen *trioxide*, nitrogen *tetroxide*, and nitrogen *pentoxide*, because for a given quantity of nitrogen the second contains twice as much oxygen as the first, the third

<sup>1</sup> Latin, *ferrum*, iron. The older names of these compounds are occasionally used; ferrous chloride being called iron protochloride, and ferric chloride, iron perchloride.

three times as much, and so on.<sup>1</sup> The prefixes mono, di, tri, tetra, and penta are derived from the Greek words for single, two, three, four, and five.

**Symbolic Notation.**—In order to economise time and labour, and for more important reasons which will be adduced presently, it is convenient to indicate the elements by symbols instead of writing their names in full. The symbols commonly used are the initial letters of the names of the elements; thus, H stands for hydrogen, O for oxygen, N for nitrogen.<sup>2</sup> When two or more elements have the same initial, that letter can only be used for one of them, and the first two letters of their names are used for the others. Thus C stands for carbon, Ca for calcium, Co for cobalt, Cu for copper.<sup>3</sup> Similarly, since S is used as the symbol for sulphur it cannot also be used for sodium. This element has had the Latinised name *Natrium* given to it, and we use its first two letters, Na, to represent sodium.

When a single letter is used as a symbol, it is always a capital; when two letters are used, the first is a capital and the second a small letter. Co stands for cobalt, but CO for a compound of carbon and oxygen. A list of the names of the known elements and the symbols which have been adopted for each will be found in the appendix (p. 216).

Not only elements, but compounds may be briefly indicated by means of this symbolic notation. It is only necessary to write next to one another the symbols for each element in the compound. For oxide of copper we put CuO, for chloride of sodium NaCl, for sulphide of iron FeS, and so on.<sup>4</sup> It will be noticed that this method has not only the merit of brevity, but it shows the composition of a substance even more clearly than the name written in full. It will presently

<sup>1</sup> These names also contain a reference to the fact that the first of the compounds contains one "atom" of oxygen in the molecule.

<sup>2</sup> The French and Italians use the names *Azote* and *Azoto* respectively for this element, and the symbol Az. *Azote* is from the Greek *ζωή*, life, and *α*, a privative particle expressing want or absence. It is that portion of the atmosphere which will not support life.

<sup>3</sup> Latin, *cuprum*.

<sup>4</sup> This much simplified statement will receive important qualifications later.

be shown that it has other and more important advantages as well.

**Laws of Chemical Combination.**—It was pointed out (p. 31) that water consists of hydrogen and oxygen. It is never composed of hydrogen and sulphur, or of oxygen and nitrogen, or of anything else, but always hydrogen and oxygen; and that these two elements are always present in the proportion of two volumes of the former to one of the latter. Owing to the difference in the density of the gases, the proportions by weight are one part of hydrogen to eight of oxygen.

When hydrogen burns in air it unites with oxygen in the proportions mentioned and forms water. Hydrogen can unite with sulphur and with other elements, but the products are not water. Hydrogen may unite with oxygen in a different proportion, but the product is not water. Similar statements may be made in regard to every chemical compound. In short, we may say that each chemical compound always contains the same elements, and these elements are always present in exactly the same proportions by weight. This universal truth is called the *Law of Definite or Constant Proportions*.<sup>1</sup>

The decomposition of calcium carbonate (p. 65) provides data for another example of this same truth. When 100 grams of the pure substance are heated they yield exactly 56 grams of calcium oxide (lime) and 44 grams of carbon dioxide. It can be further shown that the calcium oxide contains exactly 40 grams of calcium and 16 grams of oxygen, and that the carbon dioxide contains exactly 12 grams of carbon and 32 grams of oxygen. It is clear, therefore, that the 100 grams of calcium carbonate contained in all 40 grams of calcium, 12 grams of carbon, and 48 grams of oxygen. These proportions never vary.

In examining various compounds we come across many instances of bodies apparently totally distinct, but composed of the same elements. Analysis shows that in these cases the elements are present in different proportions by weight.

<sup>1</sup> Note that a "Natural Law" bears no resemblance whatever to an Act of Parliament—it includes no element of compulsion. It is simply a condensed statement of a regularity deduced from the results of many experiments.

Thus, when mercury is ground in a mortar with a small quantity of iodine moistened with methylated spirit, a dull green powder (mercurous iodide) is produced. On increasing the amount of iodine, and continuing the grinding, a bright red compound (mercuric iodide) is formed.

The combustion of carbon in excess of oxygen gives rise to the formation of carbon dioxide, but if this gas is passed over red hot carbon another oxide of carbon (carbon monoxide) is produced.

There are five compounds of nitrogen with oxygen.

Analyses of 100 parts by weight of these compounds of mercury, carbon, and nitrogen give the following results :—

Mercurous iodide : mercury, 61·16 ; iodine, 38·84.

Mercuric iodide : mercury, 44·05 ; iodine, 55·95.

Carbon monoxide : carbon, 42·85 ; oxygen, 57·15.

Carbon dioxide : carbon, 27·27 ; oxygen, 72·72.

Nitrous oxide : nitrogen, 63·63 ; oxygen, 36·36.

Nitric oxide : nitrogen, 46·6 ; oxygen, 53·3.

Nitrogen trioxide : nitrogen, 36·84 ; oxygen, 63·16.

Nitrogen peroxide : nitrogen, 30·43 ; oxygen, 69·57.

Nitrogen pentoxide : nitrogen, 25·92 ; oxygen, 74·08.

These numbers do not appear to have any definite relation to one another. But if we calculate from them the amounts of one element combining with a constant weight of the other we obtain results of great importance. They may be expressed as follows :—

Mercurous iodide : mercury, 1 ; iodine, 0·635.

Mercuric iodide : mercury, 1 ; iodine, 1·27.

Carbon monoxide : carbon, 1 ; oxygen, 1·3.

Carbon dioxide : carbon, 1 ; oxygen, 2·6.

Oxides of nitrogen (1) : nitrogen, 1 ; oxygen, 0·57.

„ „ (2) : nitrogen, 1 ; oxygen, 1·14.

„ „ (3) : nitrogen, 1 ; oxygen, 1·71.

„ „ (4) : nitrogen, 1 ; oxygen, 2·28.

„ „ (5) : nitrogen, 1 ; oxygen, 2·85.

These figures show that the weights of iodine combining

with a fixed weight of mercury are in the proportion 1 to 2 ; that the weights of oxygen combining with a fixed weight of carbon are also in the proportion 1 to 2, and that in the case of the oxides of nitrogen, a fixed weight of nitrogen unites with various weights of oxygen which are in the proportions 1, 2, 3, 4, 5.

The simple relationship here shown is not accidental nor confined to the cases mentioned ; it is a universal truth which is generally condensed into the following statement.

If any two elements, A and B, combine in more than one proportion by weight, and if we consider a fixed weight of one of them A, then the different weights of B which combine with this fixed weight of A bear a simple relation to one another ; *i.e.* they stand to one another in a ratio always capable of being expressed by *whole* numbers, which are generally small.

This statement is known as *The Law of Multiple Proportions*.

The proportions by weight in which elements combine also show another important relationship. For illustration we will take the elements hydrogen, oxygen, chlorine, and zinc, although any other elements would do equally well.

When hydrogen burns in oxygen, the elements combine in the proportion by weight of one part of hydrogen to eight of oxygen. These amounts are said to be *equivalent* to one another. Also when hydrogen combines with chlorine it does so in the proportion by weight of one part to 35.5 of chlorine, and these are said to be equivalent to one another.

Moreover, because eight parts by weight of oxygen and 35.5 of chlorine each combine with one part by weight of hydrogen, they are also said to be equivalent.

Zinc combines with both oxygen and chlorine, and will displace hydrogen from some of its compounds. The proportions are—

Zinc with oxygen : zinc, 32.5 ; oxygen, 8.

Zinc with chlorine : zinc, 32.5 ; chlorine, 35.5.

And when zinc displaces hydrogen, 32.5 parts by weight of zinc always displace one part by weight of hydrogen.

It will be seen that the relation between the weights of hydrogen, oxygen, and chlorine are the same as before, and each of them is equivalent to 32.5 parts by weight of zinc.

Of course we could state what weights of any two elements are equivalent to one another independent of any general connection, but for the sake of uniformity we compare them all with hydrogen or oxygen, since nearly every element will combine with one or other of these. We say *the* equivalent weight of an element is that amount by weight which will combine with or displace from its compounds one part by weight of hydrogen or eight parts by weight of oxygen.<sup>1</sup>

**The Atomic Theory.**—That elements combine according to the laws of definite and multiple proportions is beyond dispute. In the absence of any certain knowledge, Dalton (1808) revived an ancient hypothesis as to the nature of matter, to explain why they do so. He suggested that matter consists ultimately of minute particles, and that chemical action takes place between these particles, which are indivisible and have definite weights. These particles he called *atoms*.<sup>2</sup> The atoms of any one element are all of equal weight and are alike in every respect, but differ from those of any other element.

This hypothesis (or supposition) has never been actually proved, but it accords with all known facts; it has therefore acquired a very high degree of probability and is universally adopted. It is known as the *Atomic Theory*.

The atoms are very minute. Their absolute weights cannot therefore be determined, but it is obvious that they must bear a relation to each other very closely connected with the equivalent weights.

As a rule the atoms do not exist singly but in groups, *i.e.* in combination with each other. These groups are called *molecules*.<sup>3</sup> The molecules of an element are composed of atoms which are all of one kind.<sup>4</sup> In the molecule of a compound the atoms are of two or more different kinds.

<sup>1</sup> If one element combines with another in more proportions than one, it has more than one equivalent.

<sup>2</sup> Greek, *ἄτομος*, indivisible.

<sup>3</sup> Latin, *moles*, a heap.

<sup>4</sup> Some elements have but one atom to the molecule.



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The symbols which we have adopted to represent the elements can now be given a more definite meaning. Na, for instance, is not only a short and convenient way of writing "Sodium," but represents one atom of that element; similarly for the symbol of every other element.

It will be shown later (p. 75) that the molecule of hydrogen consists of two atoms, and that the molecule of water is composed of two atoms of hydrogen and one atom of oxygen. As we know that the proportion by weight in which these elements combine is 1 to 8, it follows that the atom of oxygen is 16 times as heavy as the atom of hydrogen. We take the atom of hydrogen as the standard and compare the atoms of all other elements with it. The number so obtained is called the *atomic weight*. The atomic weight of oxygen therefore is 16. This is *twice* the equivalent of oxygen, and every element one atom of which combines with two atoms of hydrogen will have the atomic weight double of the equivalent.

It will also be shown that the molecule of hydrochloric acid (p. 75) consists of one atom of hydrogen and one atom of chlorine, and as the proportion by weight is 1 to 35.5 the atomic weight of chlorine is 35.5. This is the same as the equivalent, because one atom of chlorine combines with one atom of hydrogen.

In all cases the equivalent of an element is either equal to the atomic weight, or is a very simple sub-multiple of it.

The atomic weights are often referred to as *combining weights*, as they express the fixed proportions by weight in which elements combine with one another.

The formulæ used to represent compounds imply more than is shown above. Thus, the composition of water is expressed by the formula  $\text{H}_2\text{O}$ , which shows not only that the compound contains hydrogen and oxygen in the proportion of 2 volumes of the former to 1 of the latter, but that the molecule of water contains two atoms of hydrogen and one of oxygen, and, knowing the atomic weights, that two parts by weight of hydrogen have combined with sixteen of oxygen.

Similarly the molecule of sodium chloride is composed of

one atom of sodium and one atom of chlorine. The formula  $\text{NaCl}$  is therefore used to represent this molecule.

The sum of the weights of the atoms in a molecule is the weight of the molecule in terms of one atom of hydrogen, *i.e.* it is the molecular weight of the compound. Thus, the atomic weight of sodium is 23, and that of chlorine 35.5, therefore the *molecular weight* of sodium chloride is  $23 + 35.5$ , *i.e.* 58.5. The molecular weight of carbon monoxide,  $\text{CO}$ , is  $12 + 16$ , *i.e.* 28; that of carbon dioxide,  $\text{CO}_2$ , is  $12 + (16 \times 2)$ , *i.e.* 44.

The molecular weights of all compounds, however complex, may be found from their known formulæ in a similar manner, *viz.* by adding together the atomic weights of the elements.

Thus, the molecular weight of calcium carbonate  $\text{CaCO}_3$  is found thus:—

	Element.	Atomic weight.	Multiple.	Total.
	Ca, Calcium	40	$\times 1 =$	40
	C, Carbon	12	$\times 1 =$	12
	3O, Oxygen	16	$\times 3 =$	48
				100

The molecular weight of the compound is 100.

**The Quantitative Nature of Chemistry.**—The importance of the facts enunciated above cannot be over estimated. Without these quantitative relationships chemistry in the modern sense would be impossible. We should never be able to tell whether a substance was pure, or, if impure, how much impurity it contained; we should not even be able to say how much of any constituent it ought to contain. The necessity of being able to undertake all the simpler calculations of chemistry will therefore be obvious.

If we wish to find the percentage composition of a compound, that is, the amount by weight of each element in 100 parts by weight of the compound, we proceed as follows:—

We write down the formula (say that of nitrate of soda) and then find the molecular weight.

Na =	23	} 85, the molecular weight.
N =	14	
3O =	$16 \times 3 = 48$	

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Thus we see that every 85 parts by weight of this compound contain 23 of sodium, 14 of nitrogen, and 48 of oxygen.

85 parts by weight of  $\text{NaNO}_3$  contain 23 of Na.

$$\begin{array}{rcccccc} 1 & & " & & " & & " & & " & & " & & \frac{23}{85} \text{ of Na} \\ 100 & & " & & " & & " & & " & & " & & \frac{23 \times 100}{85} = 27.06 \end{array}$$

$$\text{Similarly the percentage of nitrogen is } \frac{14 \times 100}{85} = 16.47$$

$$\text{and the percentage of oxygen } \frac{48 \times 100}{85} = 56.47$$


---


$$100.00$$

In like manner we can calculate the amount of each element in 17.5, or 123, or in any other number of parts by weight of the compound; the difference is that instead of multiplying by 100 we must multiply by the number given.

For example, if we wish to find the amount of each element in 59 parts by weight of potassium bichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) we have as before

$$\begin{array}{rcccccc} \text{Element.} & & \text{Atomic wt.} & & & & \\ \text{K}_2 & = & 39 & \times & 2 & = & 78 \\ \text{Cr}_2 & = & 52.5 & \times & 2 & = & 105 \\ \text{O}_7 & = & 16 & \times & 7 & = & 112 \end{array} \left. \vphantom{\begin{array}{l} 78 \\ 105 \\ 112 \end{array}} \right\} 295$$

295 parts by weight of  $\text{K}_2\text{Cr}_2\text{O}_7$  contain 78 of potassium.

$$\begin{array}{rcccccc} 1 & & " & & " & & " & & " & & " & & \frac{78}{295} \\ 59 & & " & & " & & " & & " & & " & & \frac{78 \times 59}{295} = 15.6 \end{array}$$

$$\text{Similarly the weight of chromium is } \frac{105 \times 59}{295} = 21.0$$

$$\text{and the weight of oxygen is } \frac{112 \times 59}{295} = 22.4$$


---


$$59.0$$

It will be noticed that in these calculations no mention is made of definite quantities, but merely of proportions or parts by weight. It is obvious, however, that the results of our

calculations hold in any system of weights whatever. Thus, 59 pounds of potassium bichromate contain 15.6 pounds of potassium, 21 pounds of chromium, and 22.4 pounds of oxygen. Similarly, 59 grams of this substance contain 15.6 grams of potassium, 21 grams of chromium, and 22.4 grams of oxygen.

Again, suppose it were required to find how many pounds of nitrogen are contained in 1 cwt. of sulphate of ammonia, containing 5 per cent. of impurity. Since there are 5 pounds of foreign matter in 100 pounds, there will be  $5 \times 112 \div 100 = 5.6$  pounds in 1 cwt., so that we have only  $112 - 5.6 = 106.4$  pounds of pure sulphate of ammonia in 1 cwt. of the substance.

The problem, therefore, is to find how many pounds of nitrogen are contained in this quantity. The formula is  $(\text{NH}_4)_2\text{SO}_4$ .<sup>1</sup>

$$\begin{array}{ccccccc} \text{N}_2 = 14 \times 2 & \text{H}_8 = 1 \times 8 & \text{S} = 32 & \text{O}_4 = 16 \times 4 & & & \\ = 28 & + 8 & + 32 & + 64 & = & 132 \end{array}$$

If 132 pounds of sulphate of ammonia contain 28 pounds nitrogen, 106.4 pounds will contain  $\frac{28 \times 106.4}{132} = 22.57$  pounds.

It will be seen that calculations of this kind are of great importance in connection with the practical affairs of the farmer or of any other business man who has to employ chemical materials, artificial manures, paints, cements, etc.

We have shown how to find the percentage composition of a substance when its formula is known. The chemist is more often called upon to perform the reverse operation, and from the results of analyses, which it is customary to express in percentages, to deduce the chemical formula.

A substance on analysis was found to contain :

Sodium . . . . .	27.06
Nitrogen . . . . .	16.47
Oxygen . . . . .	56.47
	<hr/>
	100.00
	<hr/>

It is required to find its formula.

<sup>1</sup>  $(\text{NH}_4)_2$  is equivalent to  $\text{N}_2\text{H}_8$ , but it is written as above for reasons given later (p. 126).

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Divide each of the percentages by the atomic weight of its element. Thus—

$$\frac{27.06}{23} = 1.176 \quad \frac{16.47}{14} = 1.176 \quad \frac{56.47}{16} = 3.529$$

This shows that the number of atoms of each element present are in the proportion

$$\text{Na, } 1.176 \quad \text{N, } 1.176 \quad \text{O, } 3.529$$

The numbers above are almost exactly in the ratio of 1, 1, and 3, and the formula of the substance is  $\text{NaNO}_3$ ; it is sodium nitrate.

**Chemical "Equations."**—The substances which take part in a chemical reaction, and the products of the reaction may all be represented by chemical formulæ, so that formulæ may be used to assist in the representation of chemical changes.

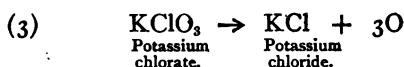
Any of the chemical changes previously described may be represented by means of formulæ. For instance, (1) the decomposition of oxide of mercury (p. 19) is written :



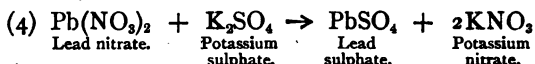
The combination of sulphur with iron :



The decomposition of potassium chlorate :



The interaction of lead nitrate and potassium sulphate when their solutions are mixed :



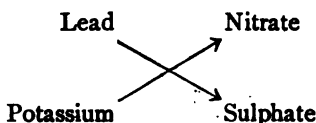
These expressions are called equations. They receive this name because the whole weight of material before and after the action must be identical.<sup>1</sup> They are not equations in the

<sup>1</sup> This, of course, is only another way of saying that in any chemical change—no matter how complex or of what kind—the total quantity of matter remains unaltered. We can neither create nor destroy matter. This universal truth is called the *Law of Conservation of Matter*.

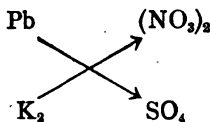
algebraical sense, and it is no longer the invariable custom to write the sign of equality (=) between the two sides, but more generally an arrow  $\rightarrow$  is used to signify the direction in which the reaction takes place. The equation  $\text{Fe} + \text{S} = \text{FeS}$  should be read, iron + sulphur yield or produce sulphide of iron, not iron + sulphur equals sulphide of iron.

Equation No. 4 represents a case of "double decomposition," *i.e.* a reaction in which two substances react, exchange parts, and thus produce two different compounds.

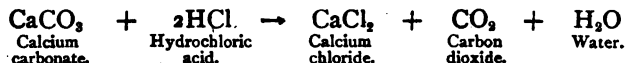
Perhaps this can be rendered clearly by a simple diagram.



Substituting the formula the expression appears thus—



Equations, however, are more convenient than this diagrammatic form for representing chemical changes. Especially is this the case when the changes are of a more complete character. For instance, to indicate the action of hydrochloric acid upon calcium carbonate by a diagram would probably prove misleading, but the change is easily represented by an equation, thus:



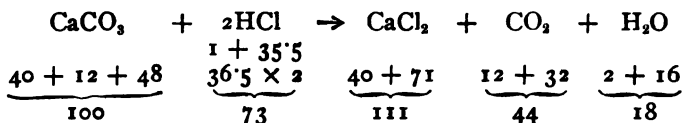
A little practice will enable any one who is familiar with the formulæ to represent all kinds of chemical changes by equations.<sup>1</sup>

The equation representing the action of calcium carbonate on hydrochloric acid illustrates the use which may be made of

<sup>1</sup> Provided also that the chemistry of the change is understood. It is easy to make up equations which "look all right" but which do not represent any chemical reaction. For instance,  $\text{Pt} + 4\text{HCl} \rightarrow \text{PtCl}_4 + 2\text{H}_2$ , may seem quite right, but such a reaction *does not take place*.

equations. They not only have the qualitative meaning mentioned above, but the quantitative significance is even more important.

They represent the amounts by weight of the materials reacting, and also the amounts by weight of the products of the reaction. In the case referred to, the equation means that one molecule of calcium carbonate reacts with two molecules of hydrochloric acid to form one molecule of each of the compounds calcium chloride, carbon dioxide, and water. But the molecular weights of each of these compounds can easily be calculated—



We now see that 100 parts by weight of calcium carbonate react with 73 parts by weight of hydrochloric acid and yield 111 parts by weight of calcium chloride, 44 of carbon dioxide, and 18 of water. The proportions in which the substances react are invariable, and so are the relative amounts of the products of the reaction.

To find out how much acid would be required if more or less than 100 parts by weight (which may be grams, pounds, tons, or anything else) of calcium carbonate are employed, and the amounts of calcium chloride and other products formed, is a simple exercise in elementary arithmetic.

**Valency.**—It will be shown (p. 75) that one atom of chlorine combines with one atom of hydrogen. In water one atom of oxygen is combined with two atoms of hydrogen, and in ammonia (p. 125) one atom of nitrogen is combined with three atoms of hydrogen. The elements chlorine, oxygen, and nitrogen are said to differ in valency.<sup>1</sup> Chlorine is described as being monovalent, oxygen as divalent, and nitrogen in ammonia is a trivalent element. Similarly carbon is a tetravalent element, for marsh gas (p. 139) is found

<sup>1</sup> Latin, *valere*, to be worth.

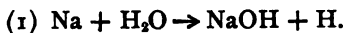
to be properly represented by the formula  $\text{CH}_4$ , *i.e.* one atom of carbon is combined with four atoms of hydrogen. A monovalent or monad element is one, of which one atom will combine with one atom of hydrogen. One atom of a divalent or diad element will combine with two atoms of hydrogen; it will also combine with two atoms of any other monad element with which it forms a compound or with one atom of another diad element. Thus one atom of oxygen will not only combine with two atoms of hydrogen but also with two atoms of potassium or sodium, which are also monad elements, or with one atom of calcium which is a diad element. In the same way one atom of a tetravalent or tetrad element will combine with four atoms of a monad element, or two of a diad element, or one atom of a diad element and two of a monad, etc. Compare, for example, the formulæ—



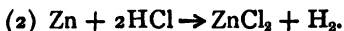
The valency of an element is measured by the number of atoms of hydrogen with which one of its atoms will unite.

If, however, the element will not combine with hydrogen we may either consider the number of atoms of oxygen with which one atom of the element will combine or determine its valency by consideration of the number of atoms of hydrogen one of its atoms will displace.

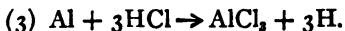
The following equations, for instance, have been found to be correct—



Sodium is therefore monovalent.



Zinc is therefore divalent.



Aluminium is therefore trivalent.

The valency of an element is in reality the number of atoms of hydrogen which one of its atoms is *worth*, either in combination or replacement.

The valency of some elements is not always the same. Phosphorus, for example, in the compound phosphine,  $\text{PH}_3$ , is



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trivalent, while in phosphorus pentoxide  $P_2O_5$  and phosphoric acid  $H_3PO_4$  it is pentavalent. Iron forms two chlorides,  $FeCl_2$  and  $FeCl_3$ . In the first of these it is obviously divalent, in the second, trivalent. The valency of sulphur shows even greater variation. In sulphuretted hydrogen,  $SH_2$ , sulphur is obviously diad; in sulphur dioxide,  $SO_2$ , it is tetrad; while in sulphur trioxide,  $SO_3$ , and sulphuric acid it is hexad.

Formulae which show plainly the valency of the elements in a compound are often employed. For use in these formulae—

A monad element would be represented thus:  $Cl-$ ,  $K-$

A diad                   "                   "                   "                    $-O-$ ,  $-Ca-$   
or  $O=$ ,  $Ca=$

and triad and tetrad elements and those of higher valency in precisely similar manner; the arrangement of the lines indicating the valency is of no importance whatever.

In this way the formulae of the following compounds would appear as in the third column:—

Caustic soda	$NaOH$	$Na-O-H$
Zinc chloride	$ZnCl_2$	$Cl-Zn-Cl$
Aluminium chloride	$AlCl_3$	$Cl-Al \begin{array}{l} \nearrow Cl \\ \searrow Cl \end{array}$
Sulphur dioxide	$SO_2$	$O=S=O$
Sulphur trioxide	$SO_3$	$O=S \begin{array}{l} \nearrow O \\ \searrow O \end{array}$
Sulphuric acid	$H_2SO_4$	$\begin{array}{c} H-O \quad \quad O \\ \quad \quad \diagdown \quad \diagup \\ \quad \quad S \\ \diagup \quad \diagdown \\ H-O \quad \quad O \end{array}$
Phosphorus pentoxide	$P_2O_5$	$\begin{array}{c} O \quad \quad O \\    \quad \quad    \\ P-O-P \\    \quad \quad    \\ O \quad \quad O \end{array}$

## CHAPTER VII

### OXIDES, ACIDS, BASES, AND SALTS

It has been shown (p. 16) that when elements combine with oxygen they form compounds known as oxides, and that on the addition of water some of these oxides pass into solution.

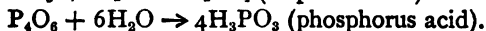
**Acids.**—The oxides of sulphur and phosphorus obtained by burning the elements in oxygen, thus dissolve in water, and in doing so impart to the water an acid reaction (it reddens blue litmus). It is not strictly accurate to say that these oxides dissolve in water; they combine with it forming soluble compounds. Such compounds are known as acids. The combination may be represented by an equation. Thus, in the case of sulphur, the oxide  $\text{SO}_2$  combines with water and forms sulphurous acid—



In the case of phosphorus, the oxide  $\text{P}_2\text{O}_5$  forms phosphoric acid—



Sulphur and phosphorus each form another oxide which will also combine with water and form an acid—



Such oxides are said to be acidic, and there is a large number of them. The oxides of carbon, silicon, boron, arsenic, and some of the oxides of nitrogen are acidic oxides. They combine with water to form acids. The acids have a sour taste and redden blue litmus.

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**Bases.**—If now certain other oxides are added to an acid, it loses its power of reddening blue litmus solution; the acid is said to be neutralised. Oxides which have the power of neutralising an acid are called basic oxides, or more shortly, bases. They are invariably the oxides of metallic substances,<sup>1</sup> copper oxide CuO, lead oxide PbO, mercury oxide HgO, calcium oxide CaO, magnesium oxide MgO, iron oxide Fe<sub>2</sub>O<sub>3</sub>, sodium oxide Na<sub>2</sub>O, potassium oxide K<sub>2</sub>O are basic oxides.

We have, therefore, two chief classes of oxides—

( $\alpha$ ) Acidic oxides, which form acids with water.

( $\beta$ ) Basic oxides, which will neutralise these acids.

Basic oxides also combine with water. The compounds formed are called hydroxides.<sup>2</sup> Some of these are soluble in water, and impart to the water the power of restoring the blue colour to reddened litmus. They are said to be alkaline.

Potassium oxide K<sub>2</sub>O combines with water.



The compound formed is very soluble in water, and the solution is strongly alkaline. It is potassium hydroxide, also known as caustic potash.

Calcium oxide (quick lime) forms calcium hydroxide (slaked lime). This is slightly soluble in water, giving the solution known as lime water; it is alkaline.

Iron oxide, Fe<sub>2</sub>O<sub>3</sub>, and copper oxide, CuO, can be obtained combined with water. The compounds are not soluble, and therefore no alkalinity is noticeable.

The basic oxides can therefore be divided into two groups, those which are soluble and those which are insoluble in water. The former are known as *alkalis*. They have a "soapy" taste, and turn blue litmus red.

**Salts.**—When a solution of an alkali is added to that of an acid they yield a neutral solution if the quantity of each is correct. This in itself would not show that anything more than mere mixing had taken place, but on evaporating nearly

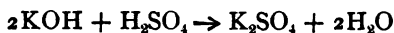
<sup>1</sup> It must not be assumed that acidic oxides are invariably the oxides of non-metals. Some metals, *e.g.* chromium, manganese, form acidic oxides.

<sup>2</sup> The term "hydroxide" might be applied also to the acids, but it is not generally so used.

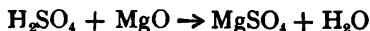
to dryness, a substance is obtained which is totally different from either the acid or the alkali. If, for example, sulphuric acid be added to caustic potash solution, until neutral, and the solution be evaporated, a white crystalline solid is obtained. Analysis shows that it is properly represented by the formula  $K_2SO_4$ ; it is known as potassium sulphate.

If we treat sulphuric acid with magnesium oxide, warming the mixture to assist solution, on evaporation a white crystalline solid is again obtained. This is magnesium sulphate,  $MgSO_4$ .<sup>1</sup> It will be seen, therefore, that when a basic oxide, whether soluble or insoluble, neutralises an acid, another compound is formed. Such compounds are called salts.

The reaction in the first case is represented by the equation—

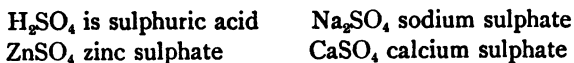


that in the second case—



The salt may be conveniently considered as arising from the combination of the basic and acidic oxides with elimination of the water with which they were combined. *Bases combine with acids to form salts, with the liberation of water.* We have shown the formation of acids from acidic oxides and water. There are several acids which are not formed in this way. Hydrochloric acid is the most familiar example. The formula of this compound is  $HCl$ . It is formed by the union of hydrogen and chlorine, and contains no oxygen. Its solution in water possesses all the properties of an acid; it has a sour taste, reddens litmus, and can be neutralised by a base such as sodium oxide or hydroxide, when it forms sodium chloride (common salt),  $NaCl$ .

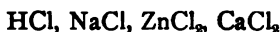
Comparing the formula of a salt with that of the acid from which it can be produced we notice great similarity, thus—



<sup>1</sup> These crystals contain water of crystallisation (p. 29); they have the formula  $MgSO_4 \cdot 7H_2O$ .

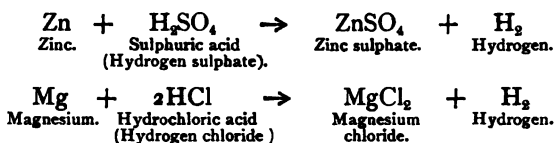
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The formulæ of the salts formed from hydrochloric acid show a like similarity—



According to these formulæ an acid differs from its salts in that in the latter the hydrogen of the acid is replaced by a metal. For this reason it is often convenient to look upon the acids as salts of hydrogen, and it is not at all unusual to find sulphuric acid referred to as hydrogen sulphate, hydrochloric acid as hydrogen chloride, and other acids in corresponding manner.

In many cases this replacement of hydrogen can be performed directly. Thus if zinc, iron, magnesium, and certain other metals are treated with dilute sulphuric or hydrochloric acid, the hydrogen is set free from the acid and the metal takes its place—



The properties of acids we have now found are—

- ( $\alpha$ ) They have a sour taste and redden blue litmus.
- ( $\beta$ ) They are neutralised by alkalies or bases, generally with the formation of a salt and liberation of water.
- ( $\gamma$ ) They contain hydrogen which can be replaced by a metal forming a salt.

In a previous experiment we found that on neutralising sulphuric acid with caustic potash, potassium sulphate,  $\text{K}_2\text{SO}_4$ , was formed. If we take the same amount of sulphuric acid and add only one-half the amount of caustic potash required to neutralise it, we obtain on evaporation another crystalline body, which analysis proves to have the composition represented by the formula  $\text{KHSO}_4$ .



This is obviously sulphuric acid in which only one-half of the hydrogen has been replaced by potassium. It has some

of the properties of an acid, and some of the properties of a salt. It is called an acid salt. The actual names applied to it are "acid potassium sulphate" alluding to its properties, or "potassium hydrogen sulphate" alluding to the elements it contains.

If we try a similar pair of experiments with hydrochloric acid we shall obtain the same compound in each case, potassium chloride,  $\text{KCl}$ . We can therefore form two sulphates, but only one chloride of potassium. Acids such as sulphuric acid, forming two salts of potash, are said to be *dibasic*. Those which like hydrochloric form only one salt are said to be *monobasic*.

The basicity of an acid is determined by the number of atoms of hydrogen which can be displaced by a metal; thus  $\text{HNO}_3$ , nitric acid, is *monobasic*;  $\text{H}_2\text{CO}_3$ , carbonic acid, is *dibasic*;  $\text{H}_3\text{PO}_4$ , orthophosphoric acid, is *tribasic*;  $\text{H}_4\text{P}_2\text{O}_7$ , pyrophosphoric acid, is *tetrabasic*. It does not always happen, however, that all the hydrogen in an acid is replaceable. Thus  $\text{H}_3\text{PO}_3$ , phosphorous acid, is *dibasic*, because only two of the three hydrogen atoms it contains are replaceable by a metal.  $\text{H}_3\text{PO}_2$ , hypophosphorous acid, is *monobasic*, for the only salt of potash which can be prepared from it is  $\text{KH}_2\text{PO}_2$  (potassium hypophosphite). In a future chapter it will be shown that  $\text{CH}_3\text{COOH}$  (acetic acid) and similar acids are also *monobasic*.

When all the replaceable hydrogen in an acid has been replaced by a metal, the salt formed is called the *normal* salt of the acid. It often happens that the normal salt is also neutral, but this is not always the case. For instance, the normal sulphate of sodium or potassium ( $\text{Na}_2\text{SO}_4$  or  $\text{K}_2\text{SO}_4$ ) is neutral; the normal phosphate ( $\text{Na}_3\text{PO}_4$ ) is strongly alkaline; while the salt  $\text{Na}_2\text{HPO}_4$  is neutral, although it contains replaceable hydrogen.

The following is perhaps the most convenient system of nomenclature for such salts:—

$\text{Na}_2\text{SO}_4$ , normal sodium sulphate. (Neutral.)

$\text{NaHSO}_4$ , sodium hydrogen sulphate. (Acid.)

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$\text{Na}_3\text{PO}_4$ , normal sodium phosphate. (Alkaline.)

$\text{Na}_2\text{HPO}_4$ , hydrogen di-sodium phosphate. (Neutral.)

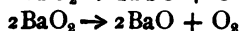
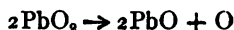
$\text{NaH}_2\text{PO}_4$ , sodium di-hydrogen phosphate. (Acid.)

*Other oxides.*—There are two other classes of oxides, in addition to those we have called acidic and basic.

### (a) Peroxides.

When lead is oxidised in the air or in oxygen it forms the oxide  $\text{PbO}$ . This is a basic oxide. But this oxide of lead can be further oxidised to  $\text{PbO}_2$ . This has more oxygen in it than the basic oxide. Such oxides are called peroxides. When heated they give off part of their oxygen and generally leave a residue of the basic oxide. Other well-known peroxides are barium peroxide,  $\text{BaO}_2$  (p. 19), and manganese dioxide,  $\text{MnO}_2$ .

The action of heat upon these substances is shown in the following equations:—



When treated with sulphuric acid peroxides yield oxygen—



When treated with hydrochloric acid they cause the liberation of chlorine, as the oxygen which might be expected to be liberated combines with the hydrogen of some of the hydrochloric acid and liberates the chlorine (p. 76)—



There are a few peroxides which behave somewhat differently. The peroxides of barium and sodium when treated with dilute sulphuric acid or hydrochloric acid yield, not water and oxygen, but hydrogen peroxide,  $\text{H}_2\text{O}_2$ —



The difference between these two classes of peroxides may be represented by graphic formulæ. Those, such as lead peroxide, which yield oxygen or chlorine when treated with sulphuric or

hydrochloric acid contain the oxygen doubly linked to the metal, thus:  $\text{Pb}_2 \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ . Those which give rise to the formation of hydrogen peroxide contain the group  $-\text{O}-\text{O}-$ ; thus sodium peroxide is  $\text{Na}-\text{O}-\text{O}-\text{Na}$ , and barium peroxide is  $\text{Ba} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ .

(b) Carbon monoxide,  $\text{CO}$ , nitric oxide,  $\text{NO}$ , do not come into the above groups, for they are neither acid nor basic, nor peroxides.

The above classification of the oxides, while useful and even necessary, must not be looked upon as rigid. Some basic oxides also act as acidic oxides in the presence of strong bases, while some acidic oxides have peroxide properties.<sup>1</sup>

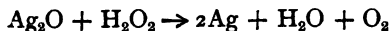
**Hydrogen Peroxide.**—As stated above, this substance is formed when barium peroxide is treated with an acid. Sulphuric acid is the most convenient as it precipitates the insoluble barium sulphate; any excess of sulphuric acid can be removed by cautious addition of barium hydroxide,  $\text{Ba}(\text{OH})_2$ , and the whole of the sulphate filtered off. The filtrate is a dilute solution of hydrogen peroxide, from which the pure material may be obtained by distillation under reduced pressure.

It is a powerful oxidising agent, rapidly giving off oxygen and leaving water. Its action upon potassium iodide is shown in the equation—



With chromic acid,  $\text{H}_2\text{CrO}_4$ , it forms a deep blue compound supposed to contain the oxide  $\text{Cr}_2\text{O}_7$ , but this decomposes so rapidly that it cannot easily be analysed. Hydrogen peroxide may also act as a reducing agent in certain special cases.

(a) Upon silver oxide the action is as follows:—



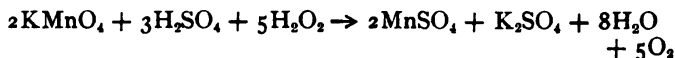
<sup>1</sup> Zinc oxide,  $\text{ZnO}$ , and aluminium oxide ( $\text{Al}_2\text{O}_3$ ) will dissolve in caustic soda or potash forming the zincate or aluminate of soda or potash.

$\text{MnO}_2$ , manganese dioxide,  $\text{CrO}_3$ , chromium trioxide, both of which show peroxide properties, will combine with bases and form salts.



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(b) Upon potassium permanganate <sup>1</sup>—



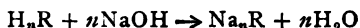
Its oxidising action is utilised for bleaching delicate materials.

## APPENDIX TO CHAPTER VII

### FURTHER CONSIDERATION OF ACIDS, BASES, AND SALTS

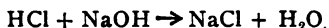
A PROPERTY of acids which provides a fairly satisfactory definition is their power of forming salts with caustic soda or potash.

An acid may be defined as a body of the formula  $\text{H}_n\text{R}$  which will react with caustic potash to form a salt of the formula  $\text{K}_n\text{R}$  according to the equation—

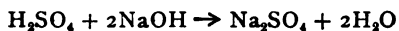


where  $n$  represents the number of replaceable hydrogen atoms in the molecule of the acid, and R the remainder of the molecule.

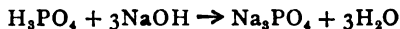
Thus in hydrochloric acid  $n$  is 1 and R is chlorine, and the equation stands—



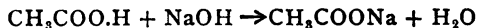
With sulphuric acid,  $n$  is 2 and R is  $\text{SO}_4$ —



With phosphoric acid,  $n$  is 3 and R is  $\text{PO}_4$ —



With acetic acid,  $n$  is 1 and R is  $\text{CH}_3\text{COO}$ —

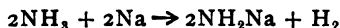


It is useless to define an acid as the compound formed by the union of an acidic acid and water, as there are many acids which contain no oxygen, *e.g.* HCl, HBr. The property of reddening blue litmus is shared by water solutions of some normal salts such as  $\text{CuSO}_4$ . The displacement of hydrogen by metals will also

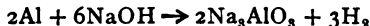
<sup>1</sup> Hydrogen peroxide is supplied in dilute solutions which are described by the amount of oxygen they will give off; thus a 20-volume solution of hydrogen peroxide is one which will give off 20 times its own volume of oxygen.

take place from substances of a totally different character, such as ammonia and caustic alkalies, thus—

Dry ammonia gas passed over heated sodium gives sodamide and hydrogen.



Aluminium<sup>1</sup> boiled with caustic soda solution gives sodium aluminate and hydrogen.



**Electrolysis<sup>2</sup> and Ionic Dissociation.**—Electrolysis consists in the separation of the components of a dissolved substance by means of a current of electricity passed through the solution. It is not every compound which can be so decomposed; those which can are called electrolytes. The apparatus necessary varies in detail with the nature of the products, but that used for the electrolysis of water (p. 31) contains all the essential parts. An electric battery is connected by wires with each of the platinum plates. These plates are obviously the means by which the current enters and leaves the solution. They are therefore known as electrodes.<sup>3</sup> That connected with the zinc of the battery is the negative electrode or kathode,<sup>4</sup> that connected with the carbon<sup>5</sup> the positive electrode or anode.<sup>6</sup>

In the electrolysis of water it was pointed out that the water alone would not conduct electricity. There are no signs of decomposition until sulphuric acid is added; then oxygen is given off at the anode and hydrogen at the kathode. Had we used copper sulphate instead of sulphuric acid we should still have had oxygen at the anode as before, but copper at the kathode. This copper must of necessity have come from the copper sulphate, not from the water, and this being so the student will probably ask himself whether the hydrogen given off during the electrolysis of water does not come after all from the acid. In a sense this is actually the case.

Independent evidence has been obtained showing that when electrolytes are dissolved in water they undergo a species of decomposition, or, more strictly, dissociation. These electrolytes are precisely those compounds which may take part in double decompositions with one another—namely, acids, salts, and bases. When sulphuric acid is in dilute solution in water it is largely dissociated

<sup>1</sup> Metallic zinc behaves in a similar manner.

<sup>2</sup> Gk. *λύσις*, a setting free.

<sup>3</sup> Gk. *ὁδός*, a way or path.

<sup>4</sup> Gk. *κάτω*, down. Kathode therefore means "the way down."

<sup>5</sup> It has been assumed a simple battery is employed consisting of zinc and carbon plates. Of course any other form would do equally well. The essential thing is that the kathode is the electrode connected with the negative terminal of the battery, and the anode that connected with the positive terminal.

<sup>6</sup> Gk. *άνω*, up. Anode therefore means "the way up," *i.e.* against the current.

into  $2\text{H}^+$  and  $\text{SO}_4$ , sodium sulphate into  $2\text{Na}$  and  $\text{SO}_4$ , caustic soda into  $\text{Na}$  and  $\text{OH}$ . According to modern theory these portions of the dissociated compound carry equal and opposite charges of electricity, the hydrogen and sodium groups being charged positively, and the  $\text{SO}_4$  and  $\text{OH}$  groups negatively. They are known as ions.<sup>2</sup> When the electrodes are connected with the terminals of the battery, the ions by virtue of their electric charges are directed towards the electrode oppositely charged; thus the hydrogen, sodium, or other metallic (positive) ions are directed to the kathode; the  $\text{SO}_4$ ,  $\text{Cl}$ , or other negative ions to the anode.

We can now see what probably happens when a current is passed through water containing an acid or a salt in solution. The current does not decompose the acid or salt. That is already dissociated by the act of solution; but in the case of dilute sulphuric acid, the hydrogen ions are directed to the kathode, and there form molecules of hydrogen which accumulate and are given off as hydrogen gas. The  $\text{SO}_4$  ions would accumulate at the anode, but for the fact that  $\text{SO}_4$  reacts with the water to form sulphuric acid and oxygen. The sulphuric acid is thus again formed and again undergoes dissociation. Indirectly, therefore, the hydrogen and oxygen given off during the electrolysis of water really come from the water although the sulphuric acid acts as an intermediary.

The case of copper sulphate is identical. The salt is dissociated into  $\text{Cu}$  and  $\text{SO}_4$ . Copper is deposited on the kathode instead of hydrogen,<sup>3</sup> and the  $\text{SO}_4$  reacts with water at the anode to form sulphuric acid and oxygen.

If sodium sulphate solution be electrolysed hydrogen is evolved at the kathode, oxygen at the anode. The ions of sodium sulphate are  $2\text{Na}^+$  and  $\text{SO}_4^{--}$ . But the sodium which might accumulate at the kathode reacts with water, giving caustic soda and hydrogen, while the  $\text{SO}_4$  gives as before  $\text{H}_2\text{SO}_4$  and oxygen. If the solution be made purple with neutral litmus that portion surrounding the kathode will be turned blue, that around the anode red.

From the foregoing it will be seen that the characteristic of an acid is that it gives hydrogen ions when in water solution; a soluble basic hydroxide gives hydroxyl ions ( $\text{OH}^+$ ). The more dilute the solution the more complete this ionisation is.

In the ionisation of acids is found the explanation of most of their properties. It gives a reason for the frequent liberation of hydrogen when certain metals act upon acids; and shows why concentrated acids behave so differently from the same acids

<sup>1</sup> These groups of atoms must not be looked upon as free hydrogen, or sodium, etc.

<sup>2</sup> From the Gk.  $\epsilon\eta\mu\iota$ , I go; the word may be taken as meaning "wanderers" or "travellers."

<sup>3</sup> A small quantity of hydrogen is also given off, and this must increase with the increasing number of hydrogen ions due to the continual formation of sulphuric acid.

diluted. Hydrogen cannot be obtained from concentrated sulphuric acid by the action of zinc or any other metal, nitric acid will only yield hydrogen on treatment with magnesium when diluted with large quantities of water, and liquid anhydrous hydrochloric acid obtained by condensing the gas by great cold and pressure has no acid properties. It also explains the reactions (double decompositions) which take place between electrolytes in solution. For instance, when solutions of sodium sulphate and barium chloride are mixed together a heavy white precipitate is thrown down.

Now, sodium sulphate is ionised into  $2\text{Na}^+$  and  $\text{SO}_4^{--}$

while barium chloride is ionised into  $\text{Ba}^{++}$  and  $2\text{Cl}^-$ .

In these circumstances the barium ion has the same opportunity of combining with the  $\text{SO}_4^{--}$  ion as the sodium ion has, and barium sulphate is therefore formed, and, being insoluble, is removed from the solution as a white precipitate.

## CHAPTER VIII

### LIMESTONE

**Calcium Carbonate.**—All forms of limestone, including chalk and marble, consist essentially of one chemical compound known as calcium carbonate or carbonate of lime, and the differences between them arise chiefly from the mode of their formation and their structure. In marble the calcium carbonate exists as a mass of minute crystals.<sup>1</sup> Chalk and most limestones are not crystalline, but yield evidence of their organic origin, in the abundant remains of shells, coral, etc., which, in the case of many limestones, form a large proportion of the rock.<sup>2</sup>

In the British Isles, true white marble is not found, but chalk and limestones exist plentifully, and in districts where they abound the industry of "lime burning," or the manufacture of "quick-lime," is almost invariably to be found.

**Lime Burning.**—An experiment in "lime burning" can easily be performed by the aid of a blow-pipe. If a weighed piece of chalk, limestone, or marble be heated strongly for some time, then allowed to cool and again weighed, it will be found to have decreased considerably in weight. If the heating be continued, the loss becomes greater until the chalk, limestone, or marble has lost 44 per cent. of its original weight. The white substance which is left is commercially known as quick-lime. A heavy gas is given off during the process; and if this gas were collected, its weight would be found to be exactly equal to the loss in weight suffered by the calcium carbonate on heating.

<sup>1</sup> Calcite or Iceland Spar is another highly crystalline form of calcium carbonate.

<sup>2</sup> The shells of birds'-eggs, coral, pearls, the shells of shell fish, also consist of calcium carbonate with varying amounts of organic material.

These facts show that the term "lime burning" is not a correct one. The change which takes place during the making of quick-lime is decomposition, while burning, is combination with oxygen. The term, however, is in general use and is unobjectionable, provided that it is looked upon merely as a technical term for a commercial process with no chemical significance attached to it.

Calcium carbonate yields, on heating, quick-lime and a gas. From the quick-lime, a metal may be extracted. This metal is hard, of a yellowish-white colour, tarnishes rapidly when exposed to the air, and decomposes water at ordinary temperatures. It is known as calcium. When calcium is heated in oxygen, it burns, and combines with the oxygen forming calcium oxide, and this compound is in every respect identical with quick-lime.

From the gas a black solid can be extracted by passing it over heated magnesium. This black solid is known as carbon. When carbon is burnt in oxygen it yields carbon dioxide; this is in every respect identical with the gas given off during lime burning.

We are now able to state the nature of the change more definitely :—

Chalk	}	when heated yields calcium oxide and carbon dioxide ;
Marble		
Limestone		

or in the form of a chemical equation—



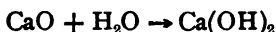
It will be noticed that instead of using the customary sign  $\rightarrow$  in this equation, we have used one with an arrow head pointing each way. This is to signify that the reaction may take place in either direction, *i.e.* it is *reversible*. It means that not only will calcium carbonate decompose into quick-lime and carbon dioxide, but also that quick-lime will combine with carbon dioxide to form calcium carbonate.<sup>1</sup> In which direction

<sup>1</sup> This will be recognised as the direct union of an acidic with a basic oxide to form a salt.

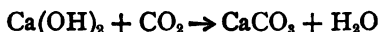
the reaction will proceed depends upon the temperature and pressure.

The decomposition of calcium carbonate is imperceptible until a temperature of about  $500^{\circ}$  C. is reached. Below this temperature the only reaction noticeable would be the combination of quick-lime with carbon dioxide. Even at temperatures above  $500^{\circ}$  C., if the calcium carbonate were heated in a closed vessel, so that the gas was not able to escape, there would exist, for any given temperature, a condition of equilibrium in which decomposition and recombination would just balance one another, and the reaction would never be completed. It is necessary therefore to remove the carbon dioxide as it is formed.

**Lime.**—One of the chief uses of quick-lime is for the making of mortar. The lime is first slaked (p. 4)—



The slaked lime is mixed with sand and water to make a paste, and in this condition is used for building purposes. Mortar, however, does not stick bricks together as gum or glue might, although mere drying may be considered the first stage in the hardening process. The actual setting depends upon the absorption of carbon dioxide from the air and the formation of calcium carbonate<sup>1</sup>—



The calcium carbonate thus formed acts as a hard cement binding the sand grains together.

Another action is said to take place slowly under ordinary conditions. White sand is a compound of the element silicon (p. 106) with oxygen ( $\text{SiO}_2$ ). It is an acidic oxide, and may possibly combine with the lime, forming calcium silicate. The formation of this compound would give additional hardness to the mortar, but the action—if it occurs at all—is extremely slow.

The combination of lime with silica takes place much

<sup>1</sup> This action must of necessity commence on the outside of the mortar and proceed inwards.

more rapidly on moderate heating, a fact which is utilised in the manufacture of the so-called lime-silica bricks. Here, the two substances are intimately mixed together, moulded into the required shape and treated with super-heated steam under pressure.

Cement is another important material of which lime is an essential constituent. Portland cement is made by mixing lime and clay in proper proportions. The mixture is heated strongly until it just begins to melt (or rather to vitrify or become glassy). The resulting "clinker" is ground to fine powder; this is the "cement." It has the power of setting hard when in contact with water, and unlike mortar does not need exposure to the air.

The most important salts of calcium are the phosphate (p. 97), chloride,  $\text{CaCl}_2$ , sulphate,  $\text{CaSO}_4$ , and silicate (p. 111).

The chloride can be obtained by dissolving calcium carbonate or hydroxide in hydrochloric acid. It is a white solid substance which, when freed from water of crystallisation, is largely used as a drying agent. It takes up water readily, and quickly becomes damp or even liquid on exposure to air through absorption of atmospheric moisture. It is used for drying gases, and for removing water from many liquids.<sup>1</sup>

Calcium Sulphate occurs fairly plentifully in nature as gypsum or alabaster ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

It can also be prepared by mixing strong solutions of a soluble sulphate and calcium chloride—



Gypsum is largely used for the manufacture of plaster of Paris. When it is heated to a temperature of  $125^\circ \text{C}$ . it loses most of its water of crystallisation and is converted into a white amorphous powder.<sup>2</sup> This is plaster of Paris. Its utility for the making of plaster casts depends upon its

<sup>1</sup>  $\text{CaCl}_2$  cannot be used for drying alcohol. It combines with this liquid as it does with water, forming a crystalline compound in which the alcohol takes the place of water of crystallisation. Alcohol must be dried with quick-lime (p. 148).

<sup>2</sup> This is probably a mixture of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , with  $(\text{CaSO}_4)_2\text{H}_2\text{O}$  and the anhydrous salt,  $\text{CaSO}_4$ .



property of hardening when mixed with water. This hardening is due to recombination with water and the consequent formation of the crystalline substance  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The crystals formed are, however, so small that the whole mass appears to the eye non-crystalline and dead-white.

When gypsum is heated too strongly it loses all its water of crystallisation, and is said to be "dead-burnt." In this condition it is useless for plaster, as it will no longer harden quickly on the addition of water.

**Calcium Carbide.**—This compound is formed by the action of carbon on quick-lime at a very high temperature—



It is used in the preparation of acetylene gas for illumination, etc. (see also p. 158).

**Carbon Dioxide.**—When chalk or any other form of calcium carbonate is treated with an acid, effervescence takes place.

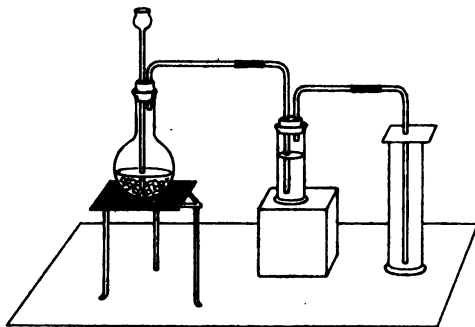


FIG. 10.

Effervescence is always due to the giving off of gas, and the gas in this case is carbon dioxide. The same gas is evolved when calcium carbonate is heated strongly, also when carbon is burnt in oxygen—

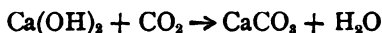


The gas may be collected by downward displacement. The apparatus generally employed is shown in Fig. 10. Into

the flask fragments of marble are placed, and dilute hydrochloric acid added by means of the funnel. The escaping gas is passed through water contained in the wash-bottle to remove all traces of hydrochloric acid, and then is collected in the gas-jar by downward displacement. To tell when the jar is full of the gas, apply a lighted taper to its mouth; the gas will immediately extinguish the taper.

Carbon dioxide is a colourless, odourless, tasteless gas; it is 22 times as dense as hydrogen (p. 34), that is, about  $1\frac{1}{2}$  times as heavy as air. It is slightly soluble in water,<sup>1</sup> and the solution is feebly acid to litmus. This is doubtless due to the formation of the unstable carbonic acid  $\text{H}_2\text{CO}_3$ , a substance which has never been prepared pure (p. 163).

The heaviness of carbon dioxide can be shown, by pouring it downwards from one jar to another, by filling soap bubbles with the gas (these rapidly descend), or by filling with it a beaker placed on the scale pan of a balance. One litre of carbon dioxide weighs 2.17 grams. If carbon dioxide be passed through lime water a white precipitate of calcium carbonate is thrown down—



This reaction is used as a test for the presence of the gas.

If the passage of the gas through the lime water is prolonged, the precipitate first formed gradually dissolves owing to the formation of a soluble calcium hydrogen carbonate—



It is owing to this action that limestone and chalk dissolve in river and spring water. These invariably contain carbon dioxide—sometimes in considerable quantities. Water thus rendered impure reacts with soap (p. 165) and prevents the formation of a lather. It is said to be hard.

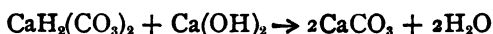
<sup>1</sup> At 760 mm. pressure and 15° C. water dissolves its own volume of carbon dioxide. A solution made under a pressure of about 3 atmospheres is known as "soda water." The relation of the solubility of a gas to pressure is given in the following statement generally known as Henry's Law. "The concentration of a saturated solution of a gas is proportional to the pressure at which the gas is supplied."

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The "hardness" thus produced may be reduced in several ways :—

(1) By boiling. The equation given above shows the action of carbon dioxide and water upon calcium carbonate as reversible. It is reversed if the water is heated, for then the calcium hydrogen carbonate is decomposed into carbon dioxide, water, and calcium carbonate. It is this redeposited calcium carbonate, which forms the "fur" or incrustation in boilers, and the thick white coating often found on the insides of kettles.

(2) By adding more lime. This is known as Clark's softening process. If slaked lime or lime water be added to water containing calcium carbonate in solution, the added lime combines with the excess of carbon dioxide. It is therefore precipitated together with the calcium carbonate previously in solution—



(3) By addition of ammonium chloride (sal ammoniac).



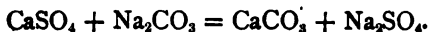
Water treated in this way could not be used for domestic purposes. It is not actually rendered soft, but the calcium is all converted into chloride, and this salt—being very soluble—does not form a "fur" in steam boilers.<sup>1</sup>

Because hardness produced by calcium carbonate is dispelled by boiling, it is said to be "temporary." Magnesium carbonate dissolves under exactly the same conditions and affects the water in precisely the same manner.

<sup>1</sup> Other methods of softening water for technical purposes are employed, among which the following should be noted :—

Certain double silicates called zeolites—which contain aluminium and alkali bases and, generally, calcium also—possess the property of exchanging the alkali for the calcium or magnesium present in hard water, and are therefore used to soften it. When the alkali is entirely replaced by calcium or magnesium, the softening power of the zeolite is exhausted; it is said, however, that it can be regenerated by treatment with sodium chloride. An artificial zeolite is sold under the name of "Permutite" for water softening. Certain colloids, such as tannin, which keep calcium carbonate in suspension, are sometimes used to prevent the formation of boiler fur.

Water may also be rendered hard by the presence of other compounds in solution, but in these cases boiling does not soften it; such hardness is said to be permanent. Calcium sulphate is the most common cause of permanent hardness. Water containing this material may be softened by the addition of sodium carbonate (washing soda), which precipitates the calcium as carbonate.



Among other substances which may produce permanent hardness would be common salt (in a solution of which soap does not dissolve) and mineral acids; the latter decompose the soap.

Carbon dioxide can be liquefied at  $0^\circ \text{C}$ . under a pressure of 35.4 atmospheres, and at ordinary atmospheric pressure the liquid produced boils at a temperature of  $-79^\circ \text{C}$ . An important point in regard to the liquefaction of gases may be illustrated by reference to carbon dioxide.

As a rule, gases may be liquefied by lowering the temperature, or by increasing the pressure, more often by both means employed at the same time. As the pressure is increased, it becomes less necessary to reduce the temperature of the gas. For every gas, however, there is a certain temperature below which it must be cooled, or no pressure, however great, will liquefy it. This is known as the critical temperature, and there is also a certain minimum pressure, which must be applied to the gas, so that any slight lowering of the temperature of the gas below the critical temperature will cause liquefaction to commence. This is known as the critical pressure. For carbon dioxide the critical temperature and pressure are  $31^\circ \text{C}$ . and 72.5 atmospheres. That is, if we had carbon dioxide in a vessel at a pressure of 72.5 atmospheres and  $31^\circ \text{C}$ ., then any slight lowering in temperature would produce liquefaction even if the pressure remained the same; and any slight increase in pressure would also cause liquefaction even if the temperature remained constant. Any slight rise in temperature would make liquefaction impossible.

Carbon dioxide as an article of commerce is sold in

wrought-iron cylinders under a pressure of 60 to 70 atmospheres, and as the temperature of the air is usually considerably below  $31^{\circ}\text{C.}$ , the carbon dioxide in the cylinder is generally liquid, and can be obtained in this state on opening the tap with which the cylinder is fitted. If the emerging jet of liquid be beaten into fine spray, it is cooled so much by its own rapid evaporation, that it freezes, and takes the form of a white snow, which evaporates slowly and without melting. Solid carbon dioxide mixed with either forms a powerful freezing mixture.

Carbon dioxide will not burn. The metals sodium, potassium, and magnesium will burn in it, combining with the oxygen and liberating carbon; but it immediately extinguishes the flames of ordinary combustibles. Similarly it will not support respiration; for this, free oxygen is necessary. It is not, however, considered poisonous, as it is possible to breathe air containing 5 per cent. of the gas without great inconvenience. As much as 6 to 8 per cent. must be present before any signs of poisonous action appear, and it is said that 25 per cent. is needed to cause actual danger to life.

The "stiffness" of rooms in which people are congregated is due not so much to the accumulation of carbon dioxide as to high temperature, the presence of excess of water vapour, and of organic material given out with respired air.<sup>1</sup>

Carbon dioxide is sometimes referred to as carbonic acid. This is not accurate; the name should be applied only to the compound  $\text{H}_2\text{CO}_3$ , the acid of which  $\text{CO}_2$  is the anhydride. Although this acid is not known in a free state many of its salts, known as carbonates, are familiar to us. The more important will be described under their respective metals.

<sup>1</sup> Expired air after removal of water vapour will generally contain  $\text{CO}_2$ ,  $3\frac{1}{2}$ -4 per cent.; oxygen, 17-16 $\frac{1}{2}$  per cent.; nitrogen, 79 $\frac{1}{2}$  per cent.

## CHAPTER IX

### COMMON SALT

**Occurrence.**—Common salt is a white crystalline solid. It exists in solution in sea water to the extent of 3·5 per cent., and in some countries is obtained from this source by evaporation. In many places, however, it occurs in large mineral deposits. In England, the chief districts are Worcestershire, Cheshire, and North Staffordshire, and in these localities it is generally obtained by allowing water to enter the salt deposit. The saturated brine is brought to the surface by means of pumps, evaporated, and the solid salt which is left is purified by recrystallisation. Often, however, it is mined, and the solid blocks of salt so obtained are known as rock salt.

Common salt is a most important mineral, not only because of the uses to which it can itself be put, but also because it is the chief source of the compounds of sodium and of chlorine. Many of these compounds are of great value in the industries and in medicine. An immense industry has therefore sprung up in connection with common salt.

**Properties.**—The appearance and taste of salt are familiar. Its solubility in water is shown in the diagram (p. 27). When pure, it is neutral to litmus, and remains dry on exposure to the air; any deliquescence is due to the presence of impurities, chiefly magnesium chloride. It is used by agriculturists as a condiment for cattle foods, and is sometimes applied to the land, but probably it has no direct manurial value. Its use for domestic purposes is due almost entirely to its value as a preservative and as a condiment.

**Spirit of Salt.**—When common salt is treated with oil of vitriol a colourless gas is given off which has a powerful irritating

odour. It fumes strongly in the air, extinguishes a burning taper, and is extremely soluble in water.<sup>1</sup> From this solution it is not possible to drive off all the gas by heating. When it is boiled a considerable amount of the gas is expelled, but a mixture boiling at  $110^{\circ}\text{C}$ . and containing 20·2 per cent. of hydrochloric acid<sup>2</sup> remains. In old times, when gases or vapours were given off they were often referred to as "spirits," and hydrochloric acid was known as "spirit of salt," because it was prepared from salt. The name is still occasionally applied to it.

The solution of the gas in water is strongly acid. The acidic properties were among the first properties of the gas which were recognised, and it consequently received the name "muriatic acid,"<sup>3</sup> *i.e.* the acid obtained from brine.

**Chlorine.**—When a concentrated solution of hydrochloric acid is treated with oxidising agents, another gas is evolved, which owing to its method of preparation was originally called oxy-muriatic acid—it was thought to be a compound of muriatic acid and oxygen. It is now known that this gas is an element, and because of its yellow-green colour, the name chlorine<sup>4</sup> has been given to it.

Chlorine has a powerful irritating odour resembling that of chloride of lime but much stronger. It cannot be breathed as it attacks the mucous membrane of the throat and nose. It is chemically a very active element; phosphorus and antimony take fire in and combine with it, forming chlorides.<sup>5</sup> If the gas is mixed with hydrogen and exposed to the action of sunlight or the light from burning magnesium, the hydrogen and chlorine combine with explosion. Diffused daylight also causes the action to take place, but more slowly.

This action is one of great importance, for the product

<sup>1</sup> At N.T.P. one volume of water dissolves 525·2 volumes of the gas and then contains 45 per cent. by weight.

<sup>2</sup> If a dilute solution is boiled, water first comes off, and the temperature gradually rises until it reaches  $110^{\circ}\text{C}$ . when the same 20·2 per cent. solution distils.

The fuming of  $\text{HCl}$  in the air is due to the great solubility of the gas in water. It dissolves in the atmospheric moisture and the solution formed condenses more readily than the moisture itself.

<sup>3</sup> Latin, *muria*, brine.

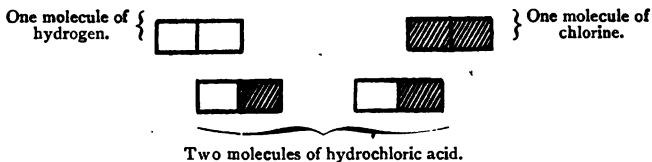
<sup>4</sup> Gk. *χλωρός*, yellow green.

<sup>5</sup> Instances of combustion without oxygen.

is the gas we have hitherto called spirit of salt or muriatic acid. It is obviously a compound of hydrogen and chlorine, and because of its acidic properties it is known as hydrochloric acid.<sup>1</sup> The combination of hydrogen and chlorine moreover helps us to find a formula for hydrochloric acid.

When equal volumes of the gases are mixed and combination takes place, the gas which is formed has *exactly the same volume as the original mixture*,<sup>2</sup> and there is none of either gas left over, i.e. if 10 c.c. of hydrogen were mixed with 10 c.c. of chlorine they would combine and form 20 c.c. of hydrochloric acid gas.

**Avogadro's hypothesis.**—"Under the same conditions of temperature and pressure, equal volumes of gases contain an equal number of molecules." This statement, known from the name of its author as Avogadro's hypothesis, although it scarcely admits of rigid proof, has been found to withstand all criticism. Assuming it to be true, then in our experiment of the combination of hydrogen and chlorine, the number of molecules after the experiment is the same as it was before. But whereas before the combination half of the molecules were chlorine and half were hydrogen, after the combination they are all molecules of hydrochloric acid. Suppose we have one molecule of hydrogen and one molecule of chlorine—that is, *two* molecules altogether—after combination we still have two molecules, but they are both molecules of hydrochloric acid. The only way in which this can be brought about is by dividing each chlorine and hydrogen molecule into two equal parts, and causing each half molecule of the one to combine with a half molecule of the other. The diagram may make this clearer.



<sup>1</sup> Also as hydrogen chloride.

<sup>2</sup> i.e. If temperature and pressure are the same as they were before the experiment.



By no method hitherto discovered has it been found possible to divide either the chlorine or hydrogen molecule into more than two parts, and therefore both of these elementary molecules are said to consist of two atoms, and the molecule of hydrochloric acid must consist of one atom of hydrogen and one of chlorine.<sup>1</sup> Hydrochloric acid is, therefore, represented by the formula HCl.

**Properties of Chlorine.**—Chlorine is a heavy gas (density 35.46 compared with hydrogen), and is therefore generally collected by downward displacement. The following experiments can be performed to demonstrate its chemical properties:—

- (a) Yellow phosphorus burns in chlorine with a pale flame forming chlorides of phosphorus,  $\text{PCl}_3$  and  $\text{PCl}_5$ .

Antimony in the form of fine powder also burns in chlorine, forming  $\text{SbCl}_3$ .

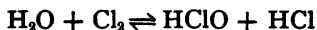
- (b) Sodium combines with the gas and forms a white solid which taste and other properties show to be common salt.
- (c) A lighted taper will burn in chlorine gas, but with a dull red and very smoky flame.
- (d) Chlorine acts on turpentine with great energy, generally causing it to take fire and deposit a large quantity of soot.
- (e) Coloured materials, such as turkey-red, litmus paper, paper with writing ink, when moistened with water are bleached by chlorine, but black printing ink, being a preparation of carbon, is not affected.

These three actions depend upon the affinity of chlorine for hydrogen. Turpentine and the wax of the taper are both compounds of carbon and hydrogen, and in each case the chlorine combines with the hydrogen forming hydrochloric acid and liberating the carbon which appears as smoke or soot.

The bleaching action of chlorine (Exp. (c)) is due to the same cause; chlorine does not bleach except in the presence

<sup>1</sup> The formula cannot be any multiple of this, say  $\text{H}_n\text{Cl}_n$ , for then the volume of the combined gases would be  $\frac{1}{n}$  of what it was when they were merely mixed.

of moisture. It combines with the hydrogen of the water forming a small quantity of hypochlorous acid and hydrochloric acid. The reaction is reversible—



Hypochlorous acid<sup>1</sup> is the immediate bleaching agent. It readily parts with its oxygen; this oxidises the colouring matter which is thereby destroyed.<sup>2</sup>

The form in which chlorine is generally used for bleaching is that of "chloride of lime" (bleaching powder). This substance is prepared by passing chlorine over slaked lime until no more of the gas is absorbed. The product is a soft, whitish powder, having an odour similar to that of chlorine. It contains  $\text{Ca}(\text{OH})_2$  and another substance generally represented by the formula  $\text{CaOCl}_2$ , which as regards the quantities of the elements present is equivalent to a mixture of (calcium chloride)  $\text{CaCl}_2$  and (calcium hypochlorite)  $\text{Ca}(\text{OCl})_2$ ,<sup>3</sup> and in a solution in water these compounds are present. It is clear, however, that bleaching powder cannot be a mixture of these. If it were, the large amount of calcium chloride present would make it very deliquescent, which it is not. It bleaches by means of the hypochlorite formed with water.

Only coarse materials can with safety be bleached with chlorine or bleaching powder. More delicate fabrics, such as linen, silk, etc., would be seriously injured.

The use of chlorine and chloride of lime is not confined to bleaching; the substances are used as powerful deodorizers and disinfectants, this action being also due to oxidation in the presence of moisture.

Chlorine is moderately soluble in water; the solution has a faintly yellow colour and is known as chlorine water. It is not very stable. Traces of hypochlorous acid and hydrochloric acid are formed, and under the influence of sunlight the

<sup>1</sup> Four oxyacids of chlorine are known:  $\text{HClO}$ , hypochlorous acid;  $\text{HClO}_2$ , chlorous acid;  $\text{HClO}_3$ , chloric acid;  $\text{HClO}_4$ , perchloric acid. It will be seen the nomenclature for these acids is similar to that we have used for oxides and other compounds. The prefix "hypo" is from the Greek ὑπο, under, and is applied to the acid containing less oxygen than the "ous" compound. This nomenclature is regularly employed.

<sup>2</sup> Note that bleaching by chlorine is a process of oxidation,

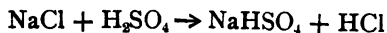
<sup>3</sup>  $\text{CaCl}_2 + \text{Ca}(\text{OCl})_2 = \text{Ca}_2\text{O}_2\text{Cl}_4 = 2\text{CaOCl}_2$ .

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hypochlorous acid loses oxygen, forming hydrochloric acid. Unless therefore chlorine water is kept in the dark it gradually changes into hydrochloric acid with the liberation of oxygen gas.

Having dealt with both the elements present in hydrochloric acid, and established its formula, it is now possible to study the properties of the acid itself with greater accuracy.

As previously stated, it is prepared by the action of sulphuric acid upon common salt—

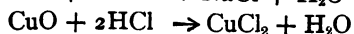
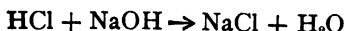


At a high temperature a larger quantity of common salt may be decomposed by the same amount of acid—

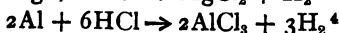
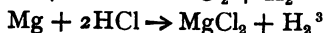
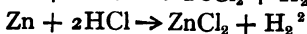
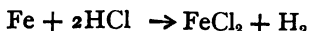


The hydrochloric acid must be collected either over mercury or by downward displacement (its density compared with air is 1.23).

**Properties of Hydrochloric Acid.**—(1) It can be neutralized by bases, when it forms salts and liberates water—



(2) Certain metals, notably zinc, iron, magnesium, and aluminium, dissolve in solutions of hydrochloric acid, liberating hydrogen and forming chlorides, which can be obtained by evaporation of the solution—

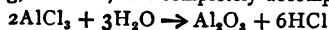


<sup>1</sup> Any other chloride would act in the same manner—in fact, the liberation of HCl with sulphuric acid is used as a test for chlorides.

<sup>2</sup> If the aqueous solution of zinc chloride be evaporated, the salt is acted upon by the water forming a basic chloride,  $\text{Zn}_2\text{OCl}_2$ .  $\text{ZnCl}_2$  can be obtained by evaporation in presence of excess of HCl.

<sup>3</sup> Magnesium chloride may be obtained on evaporation as a deliquescent crystalline solid,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . When, however, this substance is heated it is partly decomposed, some magnesium oxide being formed.

<sup>4</sup> If the solution be allowed to evaporate spontaneously  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  is formed. On heating, however, it is completely decomposed—



Action by water in the manner of these three examples is known as hydrolysis.

Hydrochloric acid may be liquefied by pressure alone. The anhydrous liquid shows no acid properties, and will not conduct electricity, thereby differing from the solution in water.

**The Halogens.**—The power of forming an acid and salts with hydrogen or a metal only is not confined to chlorine but is shared by a group of closely allied elements, bromine, iodine, and fluorine (p. 112), and these, with chlorine, because of their salt forming properties, have been called the halogens.<sup>1</sup> The acids are hydrobromic, hydriodic, and hydrofluoric acids, HBr, HI, H<sub>2</sub>F<sub>2</sub>, and the salts are known KBr, KI, KHF<sub>2</sub>, KF, respectively as bromides, chlorides, and iodides. They are monobasic acids with the exception of hydrofluoric acid, which is dibasic, as is shown by the fact that it forms two salts with potassium.

**The Oxidation of Hydrochloric Acid.**—This leads, as already stated, to the liberation of chlorine—



(1) If air or oxygen is mixed with hydrochloric acid gas but little action takes place even when the gases are strongly heated. A commercial method of preparing chlorine by the oxidation of HCl with free oxygen has, however, been devised. It is known as Deacon's process, and depends for its effectiveness upon the presence of a catalytic<sup>2</sup> agent; in this case cupric chloride, or sulphate. Hydrogen chloride gas mixed with air is passed over bricks, or other porous material, which have been soaked in a solution of the copper salt, dried, and heated strongly while the gases are being passed over them. Under these conditions oxidation of the hydrochloric acid takes place and a considerable amount of chlorine is produced.

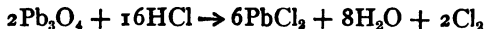
(2) By the action of manganese dioxide—



<sup>1</sup> Gk. ἅλα, salt; γεννᾶω, I produce.

<sup>2</sup> Gk. κατα, down; λύσις, a loosening. A catalytic agent is one which assists other substances to react, without itself undergoing any apparent change. The action of manganese dioxide and iron oxide in assisting the liberation of oxygen from potassium chlorate is another instance of catalysis (p. 19).

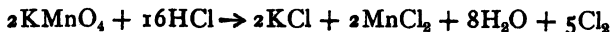
(3) By the action of red lead—



(4) By the action of potassium bichromate—



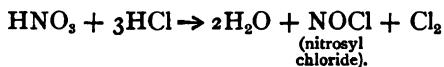
(5) By the action of potassium permanganate—



All these oxidizing agents could be used for preparing chlorine from hydrochloric acid, and in fact, with the exception of red lead, are often used.

(6) By the action of nitric acid.

Neither nitric acid nor hydrochloric acid is alone capable of acting upon such metals as gold or platinum, but a mixture of the two acids dissolve them both. This is due to the fact that nitric acid, like other oxidising agents, liberates chlorine from hydrochloric acid—

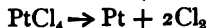


It is the free chlorine which attacks the metal, and the chloride is formed in each case. Because these mixed acids can dissolve gold, called in early times a "noble" metal, the name *Aqua Regia* has been given to the mixture.

In order to obtain chlorine from a chloride it is not necessary first to prepare hydrochloric acid and then oxidise it. If a mixture of the chloride, manganese dioxide, and sulphuric acid be employed, both changes take place simultaneously—



As a rule, however, chlorides of metals are stable substances, but certain chlorides such as those of gold and platinum decompose on heating, leaving the metal—



unaffected by heating.

**Sodium.**—This is the other element present in common salt. It is a bright whitish metal which rapidly tarnishes in moist air, so light that it floats on water and soft enough to be cut

with a knife. It decomposes water with the formation of caustic soda (sodium hydroxide)—



and forms a salt with every known acid. Practically all of these salts are soluble in water.

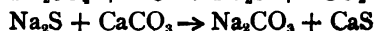
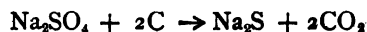
The salts of sodium are largely used in the industries and in medicine. The following are the more important:—

*Sodium Carbonate.*—This salt is sold in crystals as “washing soda” or soda crystals. There are two important methods in use for its manufacture.

(a) The Le Blanc process.

Common salt is treated in a special furnace with sulphuric acid, by which it is converted into sodium sulphate and hydrochloric acid is set free. The hydrochloric acid is caused to pass up tall “scrubbing towers” down which water is trickling, so that it is completely dissolved. The resulting solution is used as crude hydrochloric acid.

The sodium sulphate forms a white mass, which is technically known as salt cake. It is mixed with carbon (powdered coke) and calcium carbonate and heated strongly—



The mixture, which is black through excess of carbon and therefore known as black ash, is lixiviated with water, in which calcium sulphide is not readily soluble, and the solution of sodium carbonate thus obtained is evaporated. The crystals of sodium carbonate which separate have the formula,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . These crystals are very efflorescent.

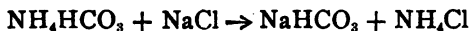
(b) The Solvay process.

The Le Blanc process is still used because of the value of the bye products, sodium sulphate and hydrochloric acid, but a much purer carbonate may be obtained by the Solvay or ammonia soda process. In this, carbon dioxide is passed through a solution of common salt saturated with ammonia. The carbon dioxide reacts with the ammonia and water to form ammonium hydrogen carbonate—



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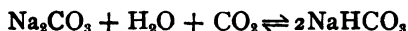
This compound reacts with the sodium chloride, forming sodium hydrogen carbonate—



which being less soluble in water separates and is collected. It is then heated strongly, when it decomposes and leaves sodium carbonate—



The compound  $\text{NaHCO}_3$  may also be prepared by passing carbon dioxide through a solution of sodium carbonate—



As shown above, this compound is decomposed on heating. It is sold under the name of sodium bicarbonate, and is largely used in medicine and in the making of baking powder.

*Sodium sulphate.* This salt also crystallises from water, solution in white efflorescent crystals having the composition  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . It is known as Glauber's salt.

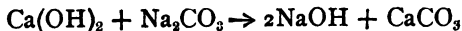
*Sodium sulphite* occurs as white efflorescent crystals,  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$  (p. 87).

*Sodium thiosulphate*,  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  (the "hypo" of the photographer).

*Sodium nitrate*,  $\text{NaNO}_3$ , Chili saltpetre, used as a nitrogenous manure (p. 132).

*Sodium silicate*,  $\text{Na}_2\text{SiO}_3$ , water glass, used for fireproofing wood and other materials, and also as an egg preservative (p. 106).

*Caustic soda*, sodium hydroxide, is not usually made by the action of sodium upon water but by the interaction of slaked lime upon sodium carbonate—



The calcium carbonate being insoluble separates from the mixture and the clear solution of sodium hydroxide is evaporated to dryness.

*Sodium pyroborate*,  $\text{Na}_2\text{B}_4\text{O}_7$ , borax (p. 114).

## CHAPTER X

### SULPHUR

**Occurrence.**—The element sulphur is very widely distributed in nature. It occurs both free and in combination. Free, it is often found in volcanic districts, where it exists as a yellow crystalline material. For a long time the world's chief supply was derived from the sulphur mines of Etna. Now, however, large quantities are obtained from the United States. A deposit of native sulphur was discovered in 1865 in the State of Louisiana, but the difficulties of mining it were not overcome until much more recently. The sulphur is now obtained by sending down water heated under pressure to a temperature of  $385^{\circ}$  F. ( $196^{\circ}$  C.). This melts the sulphur, which is brought to the surface by means of pumps.

In combination, sulphur occurs both as sulphides and sulphates, the former often providing valuable ores of the metals. The more important are lead sulphide (Galena),  $\text{PbS}$ , zinc sulphide (Blende),  $\text{ZnS}$ , mercuric sulphide (Cinnabar),  $\text{HgS}$ , copper pyrites,  $\text{CuFeS}_2$ . Iron pyrites,  $\text{FeS}_2$ , another sulphide, occurs in large quantities. It is chiefly used in the manufacture of sulphuric acid.

Calcium sulphate (p. 67) is the only sulphate which occurs in nature in really large quantities. Barium sulphate ( $\text{BaSO}_4$ ), known as barytes or heavy spar, is also of somewhat frequent occurrence, and is largely used both as a source of the compounds of barium and also as a constituent of many white paints. Potassium sulphate occurs in the salt deposits of Stassfurt in Germany. Sodium sulphate and magnesium sulphate are frequently found in the waters of mineral springs.

**Modifications.**—Sulphur as an article of commerce is



generally supplied cast in thick sticks or rolls and known as roll sulphur, also as a fine powder known as flowers of sulphur, and as milk of sulphur. Roll sulphur is a yellow, brittle solid. When gently heated it melts at  $120^{\circ}\text{C}$ ,<sup>1</sup> forming mobile pale yellow (amber-coloured) liquid. At  $160^{\circ}\text{C}$ . the liquid undergoes change in colour and consistency, becoming almost black, and so viscous that it cannot be poured out of the vessel. At  $260^{\circ}\text{C}$ ., without changing colour, it becomes less viscous, and at  $445^{\circ}$  it boils, giving off a vapour which condenses again to a pale yellow solid.

If melted sulphur be cooled slowly it assumes a crystalline form. This is seen when the thin crust which forms on the surface is broken, and the still liquid portion of the sulphur is poured out. The crust is then removed, and a mass of translucent crystals, long and needle-like in form, is found underneath. This is the prismatic or monoclinic form of crystalline sulphur. These crystals are, however, only permanent if kept above  $96^{\circ}\text{C}$ . At lower temperatures they undergo change, and in a few days lose their translucent appearance and become pale yellow and opaque. Each long prismatic crystal is changed into a mass of small crystals of a different shape. The crystalline form thus obtained is that which is permanent at ordinary temperatures.<sup>2</sup> It may be prepared more conveniently by crystallising sulphur from solution in carbon bisulphide. If roll sulphur be treated with this liquid, it will almost entirely dissolve, and a clear yellow solution will be formed, which on evaporation yields octohedral<sup>3</sup> crystals. If, instead of being allowed to cool slowly, boiling sulphur is poured into cold water, by which it is cooled too rapidly to allow crystals to be formed, it becomes converted into an elastic modification sometimes known as "plastic sulphur."<sup>4</sup> It is amorphous<sup>5</sup> (*i.e.* non-crystalline) and insoluble in carbon

<sup>1</sup> The two crystalline forms of sulphur have different melting points, the octohedral form melting at  $115^{\circ}\text{C}$ . and the prismatic at  $120^{\circ}\text{C}$ . Above  $96^{\circ}\text{C}$ . the octohedral sulphur is converted into the prismatic variety.

<sup>2</sup> It is therefore the form in which free sulphur occurs in nature.

<sup>3</sup> An octohedron is a solid figure having eight triangular faces.

<sup>4</sup> This transformation does not seem to take place with perfectly pure sulphur.

<sup>5</sup> Gk.  $\mu\omicron\rho\phi\eta$ , form ;  $\delta$ , privative particle.

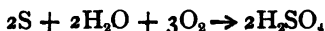
bisulphide. After a few days this form also becomes opaque and brittle, and is then found to have largely changed into the octohedral variety, but a considerable proportion remains in an amorphous condition.

Milk of sulphur is a very finely divided amorphous form of the element, thrown down from aqueous solutions of polysulphides or thiosulphates when they are treated with acids. It can be prepared readily, by boiling sulphur with milk of lime or caustic soda, in which it gradually dissolves, forming a yellow solution which contains a mixture of sulphides and thiosulphate of calcium or sodium. On the addition of an acid—preferably hydrochloric—milk of sulphur is thrown down as an almost white precipitate. It is insoluble in carbon bisulphide.

“Flowers of sulphur” is the name given to the condensed vapour of sulphur.

From the foregoing it will be seen that pure sulphur may exist in several different forms, a property which is shared by certain other elements, *e.g.* oxygen, phosphorus, and carbon (*q.v.*). This property is known as allotropy.<sup>1</sup>

**Oxides and Acids.**—Sulphur is quite insoluble in water, but if finely powdered sulphur be moistened and exposed to the air, the water will, in a short time, show the presence of sulphuric acid—



When sulphur is burned in a known volume of oxygen, *e.g.* as shown in Fig. 11, the resulting gas (sulphur dioxide), after being allowed to cool and brought to the original pressure, occupies exactly the same volume as the oxygen did. The number of molecules is therefore unchanged,<sup>2</sup> *i.e.* for every molecule of oxygen used, there is now a molecule of sulphur dioxide. Each molecule of sulphur dioxide must therefore contain one molecule of oxygen. But the molecule of oxygen contains two atoms, therefore each molecule of sulphur dioxide contains two atoms of oxygen. This, however, does not show how many atoms of sulphur there are in the molecule.

<sup>1</sup> Gk. *ἄλλος*, another; *τρόπος*, manner, form. See note on Allotropy at the end of this chapter.

<sup>2</sup> Avogadro's hypothesis.

In order to determine this, it is necessary to ascertain the density of the gas, which is found to be 32 (*i.e.* it is 32 times as heavy as an equal volume of hydrogen). But the density of a gas is one-half of its molecular weight,<sup>1</sup> and, therefore, the molecular weight of sulphur dioxide is 64. The atomic weight of sulphur is 32, that of oxygen 16, and, therefore, as two atoms of oxygen equal 32; this leaves 32 for all the sulphur present, which is exactly the weight of an atom of sulphur in terms of one atom of hydrogen. There is, therefore, one atom of sulphur in the molecule of sulphur dioxide, and its formula is  $\text{SO}_2$ .

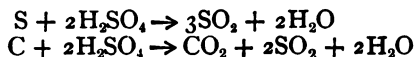


FIG. 11.

Burning sulphur in oxygen is not the only method of preparing sulphur dioxide; it is often obtained by heating concentrated sulphuric acid with copper, when a reaction takes place which is represented by the equation—



Other metals, such as silver and mercury, act in the same way. A similar reaction takes place when sulphur or carbon is heated with sulphuric acid—



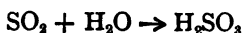
Sulphur dioxide cannot be collected over water as it is soluble, so the method of downward displacement is generally employed, as in the case of chlorine. It extinguishes a lighted taper, will not burn, and does not produce any precipitate with

<sup>1</sup> This is true for all gases, for it simply depends upon the fact that the molecule of hydrogen consists of two atoms.

Equal volumes of gases contain equal numbers of molecules (temperature and pressure being the same), therefore the density of gases are proportional to their molecular weights. We compare all these densities with hydrogen as unity. Now the molecular weight of hydrogen is 2, and if the molecular weight of a gas is  $M$ , the densities of the gas and of hydrogen are in the proportion  $M$  to 2, that is, the gas is  $\frac{M}{2}$  times as heavy as hydrogen; and in general the density of a gas is one-half of its molecular weight. (See note at the end of this Chapter.)

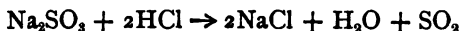
lime water. The solution in water is acid and smells strongly of the gas.

Sulphur dioxide is, therefore, an acidic oxide; the acid is present in the solution, and is known as *sulphurous acid*.<sup>1</sup>



Because the gas forms this acid with water it is often referred to as sulphurous anhydride.<sup>2</sup>

Sulphurous acid is a dibasic acid. It forms two salts with soda, the normal salt occurring in crystals of the formula  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ . Sodium hydrogen sulphite,  $\text{NaHSO}_3$ , is a white non-crystalline powder. All sulphites when treated with dilute hydrochloric or sulphuric acid give off sulphur dioxide—



Sulphurous acid, or moist sulphur dioxide, is largely used for bleaching such material as wood, straw, wool, and silk. The colouring matter often forms colourless material with the acid, or may be, in some cases, completely destroyed. Dilute hydrochloric acid or sulphuric acid will sometimes restore the colour.

Sulphurous acid is a reducing agent. It is slowly oxidised by free oxygen, but will rapidly withdraw oxygen from oxygen compounds. It will remove oxygen from water if something else is present with which the liberated hydrogen may combine.<sup>3</sup> In this manner it decolorises iodine solution—



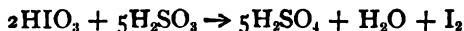
Sulphur dioxide or sulphurous acid may readily be recognised by its odour or by its reducing action. A piece of paper coloured yellow with a solution of potassium chromate turns green owing to the formation of a chromic compound. A still more delicate test is provided by a piece of paper dipped in a solution of potassium iodate and starch. A very minute amount of sulphur dioxide will cause the paper to turn blue

<sup>1</sup> The sulphur dioxide is completely driven off from solution by boiling.

<sup>2</sup> The term "Anhydride" is often applied to acidic oxides; it means an acid minus water.

<sup>3</sup> In this case sulphurous acid would appear to reduce by adding hydrogen rather than by taking away oxygen.

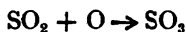
owing to the liberation of iodine and the combination of this iodine with the starch—



The oxidation of a solution of sulphur dioxide may be retarded by the addition of small quantities of alcohol, glycerine, or sugar.<sup>1</sup>

**Sulphuric Acid.**—This is, perhaps, the most important acid known in commerce. It is made in this and other countries to the extent of many thousands of tons yearly. The method of manufacture consists essentially in the oxidation of sulphurous acid; but the action of free oxygen alone is much too slow.

The acid may be prepared from its anhydride sulphur trioxide,  $\text{SO}_3$ , by the addition of water. Although dry sulphur dioxide does not combine with oxygen under ordinary conditions, its oxidation may be brought about in contact with certain porous substances, such as porcelain, ferric oxide, and particularly platinum in a finely divided condition. When sulphur dioxide and oxygen are passed together over the latter substance,<sup>2</sup> heated to a temperature of  $400^\circ \text{C.}$ , they unite, and sulphur trioxide is formed—



Sulphur trioxide is a white crystalline substance<sup>3</sup> which dissolves in water very readily, evolving much heat and yielding sulphuric acid—



To preserve it, it must be kept in sealed glass tubes.

In the common commercial method for the preparation of sulphuric acid, nitric acid or one of the oxides of nitrogen is used as the oxidising agent. The sulphur dioxide is obtained either by burning sulphur itself or more usually by the combustion of iron pyrites,  $\text{FeS}_2$ . The mixture of sulphur dioxide and air passes through a long pipe or flue, in which any solid particles are deposited, and from this, up a tower (the Glover

<sup>1</sup> The preservative apparently undergoes no change.

<sup>2</sup> The platinum remains unchanged.

<sup>3</sup> This contains a trace of moisture. The perfectly pure trioxide is a liquid which solidifies at about  $14^\circ \text{C.}$

Tower), down which crude sulphuric acid, obtained as shown later, is flowing. The mixture of the hot gases with the cold acid cools them, concentrates the acid, and also frees it from the oxides of nitrogen it contains. From the tower the mixed gases ( $\text{SO}_2$ , air, and oxides of nitrogen) pass into a series of large leaden<sup>1</sup> chambers, where they are mixed with steam and vapours of nitric acid, obtained by treating commercial sodium nitrate with concentrated sulphuric acid. The nitric acid is reduced, giving up some of its oxygen to the sulphur dioxide, thus forming sulphuric acid—



The  $\text{N}_2\text{O}_3$  (nitrous anhydride) is capable of oxidising more sulphur dioxide to sulphuric acid. As, however, nitrous anhydride is unstable and in the gaseous state consists largely of nitrogen peroxide,  $\text{NO}_2$ , and nitric oxide,  $\text{NO}$ , it is convenient to express the reaction in terms of these oxides.

The nitrogen peroxide oxidises the sulphur dioxide, causing the formation of sulphuric acid—



But nitric oxide readily takes up free oxygen from the air (p. 137), again forming nitrogen peroxide, which will effect the oxidation of a further quantity of sulphur dioxide.

From this it would seem that a small amount of nitric acid would oxidise an unlimited quantity of sulphur dioxide; but there is also a certain loss by reduction of some of the nitrogen compounds to nitrous oxide  $\text{N}_2\text{O}$  (p. 137). A still greater loss would arise by the carrying away of the excess of oxides of nitrogen from the last of the leaden chambers by the current of waste gases (chiefly atmospheric nitrogen) were it not that they are made to pass up a second tower (the Gay-Lussac tower), down which concentrated sulphuric acid is flowing. The acid absorbs the oxides of nitrogen. This acid is then sent by means of pumps to the Glover tower, where it meets with fresh sulphur dioxide, and the chain of reactions again commences.

<sup>1</sup> Lead is not acted upon by sulphuric acid to any great extent.

The sulphuric acid obtained by this process is concentrated by heating, when it forms a colourless, oily, extremely corrosive liquid. It rapidly absorbs moisture, and is therefore often used for drying gases. When mixed with water considerable contraction in volume occurs, and much heat is evolved. This may be demonstrated by taking a long glass tube of about  $\frac{1}{2}$  inch diameter, and pouring concentrated sulphuric acid into it, to the extent of about one-third of the length of the tube, and then nearly filling up with water; the level of the top of the water should be marked with an indiarubber ring. The two liquids at first do not mix owing to the great density of the sulphuric acid (1.8 compared with water as unity). If now the tube be closed with an indiarubber stopper and the liquids thoroughly mixed, the tube becomes too hot to be held in the hand, and the volume of liquid considerably smaller.<sup>1</sup>

Sulphuric acid, however, shows its affinity for water even more strongly in its action upon wood, etc. Wood and many other organic substances rapidly char, owing to the extraction of the elements of water. Consequently, it has a strong corrosive action on organic tissues. Taken internally it would cause death; externally, it produces painful wounds.

Sulphuric acid is a dibasic acid, and forms two salts of soda,  $\text{Na}_2\text{SO}_4$  (p. 82) and  $\text{NaHSO}_4$ , sodium hydrogen sulphate, often called sodium bisulphate. Most of the sulphates are soluble in water, the exceptions being those of lead, silver, and calcium, which are only slightly soluble, and those of strontium and barium.<sup>2</sup>

When sulphates are heated with charcoal they are reduced to sulphides (p. 81).

When ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (p. 200), is strongly heated in the air it is oxidised and decomposed, and sulphur trioxide is evolved—



The sulphur trioxide combines with the water, which is also given off to form an acid of approximately the composition

<sup>1</sup> Care must be taken in diluting concentrated sulphuric acid with water; it is always advisable to add the acid to the water.

<sup>2</sup>  $\text{BaSO}_4$  is almost completely insoluble in pure water.

$\text{H}_2\text{S}_2\text{O}_7$ . This acid is the original "Oil of Vitriol"; it gives off sulphur trioxide as white fumes on being heated gently, and is therefore called fuming sulphuric acid. When more water is added it forms ordinary sulphuric acid. A salt of the acid can, however, be prepared by the action of heat upon the acid sulphates—



Because they are produced by the action of heat, these salts are called pyrosulphates and the acid<sup>1</sup> pyrosulphuric acid (or disulphuric acid).

**Sulphuretted Hydrogen.**—If iron filings and sulphur be mixed together, and the mixture treated with dilute acid, hydrogen is evolved, the sulphur present taking no part in the action. If the iron filings and sulphur are heated and made to combine, and then treated with dilute acid, the hydrogen comes off combined with sulphur. The compound is a colourless gas, having a most objectionable odour of putrid eggs. Its density compared with hydrogen is 17, and therefore its molecular weight is 34; this, together with analysis of the gas, has fixed its formula as  $\text{H}_2\text{S}$ . It is known as hydrogen sulphide, or sulphuretted hydrogen. The gas burns with a blue flame similar to that of burning sulphur; the products of combustion are sulphur dioxide and water. It is soluble in water, to which it imparts a slightly acid reaction.

Sulphuretted hydrogen may be formed by passing hydrogen over sulphur at a temperature of  $310^\circ \text{C}$ ., but it is generally produced by acting upon certain sulphides with dilute hydrochloric acid. Ferrous sulphide is generally employed, because it is the least expensive.

The gas is very useful in chemical analysis, as, on being

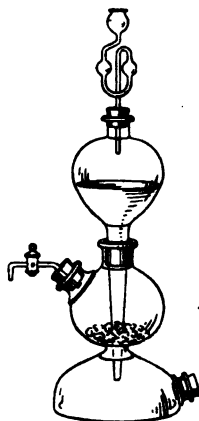


FIG. 12.

<sup>1</sup> Gk.  $\pi\acute{\upsilon}\rho$ , fire.

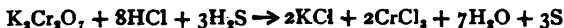


added to solutions of metallic salts, it precipitates insoluble sulphides—



As large quantities are often required, the apparatus (Kipp's apparatus) shown in Fig. 12 is generally used for its preparation. This apparatus has the advantage of causing the action of the acid on the sulphide to cease when the gas is not required and the tap is therefore closed.

Sulphuretted hydrogen is a powerful reducing agent. Owing to this property it cannot be dried by passing through sulphuric acid, as the acid is reduced by it, sulphur dioxide and sulphur being formed—



Most metals, including silver, become coated with sulphide when exposed to the action of the gas.<sup>1</sup>

Sulphuretted hydrogen is an acid, like hydrochloric acid, in that it contains no oxygen, and its solution in water is sometimes called hydrosulphuric acid. It is a dibasic acid, and forms two salts with soda, NaHS and Na<sub>2</sub>S.

The sulphides of sodium, potassium, and ammonium, are soluble in water.

Those of calcium, magnesium, strontium, barium, chromium, and aluminium are decomposed by water, yielding hydroxides.

Those of the remaining commoner metals are insoluble in water.

**Allotropy.**—Elements which exist in several forms differing in their chemical and physical properties and often in appearance are said to show "allotropy."

The various allotropic modifications of an element differ in the amount of energy they contain, and therefore in their powers of reacting with other substances.

The preparation and properties of *ozone* throw light on

<sup>1</sup> A similar action takes place with other sulphur compounds, such as albumen (white of egg) or vulcanised indiarubber, both of which contain sulphur.

the nature of allotropy. It was mentioned that this substance is formed when dry oxygen is subjected to the action of the electric spark, or, better, to that of the silent electric discharge. The apparatus necessary for this latter method of preparation is shown in the illustration.

The central space C in the apparatus is bounded by two glass tubes, both of which are coated with some electrical conductor, and connections are made to the terminals of an induction machine as shown. Oxygen is supplied by the side tube A, passes through the space C, and emerges from the tube B. During the passage it has become ozonised, that is, partly converted into ozone; its volume has decreased and its oxidising properties greatly intensified. It has a strong odour,<sup>1</sup> bleaches organic colouring matter, blackens a piece of silver held in it, covering the metal with a coating of oxide; liberates iodine from potassium iodide, oxidises mercury, and rapidly causes the resinification of certain oils and of turpentine.

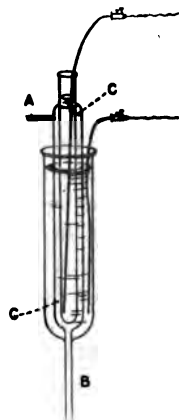


FIG. 13.

When passed through a heated tube its volume is restored to that of the original oxygen, and it loses all its specific properties; it is reconverted into oxygen.

The above method of preparation and decomposition shows that ozone consists entirely of oxygen. But as it cannot be produced pure in this way its composition can only be determined indirectly. This has been done as follows:—

A known volume of ozonised oxygen is divided into two equal portions, A and B.

A is treated with turpentine, which absorbs the ozone.

The contraction in volume shows the amount of ozone present.

B is heated, and the proper corrections having been made for temperature and pressure, the increase in volume is measured.

<sup>1</sup> This property gives it its name. Gk. *ὄζω*, to smell.

This increase is due to the conversion into oxygen of the same amount of ozone as was present in A. It is found to be one-half of the volume, as determined by the turpentine absorption.

The experiments therefore show that ozone, on being converted into oxygen, increases its volume by one-half, that is, every two volumes of ozone become three of oxygen. Therefore every two molecules of ozone become three of oxygen; but three molecules of oxygen contain six atoms, and therefore every molecule of ozone contains three atoms of oxygen. It is represented by the formula  $O_3$ . Ozone is therefore an allotropic form of oxygen, differing from the ordinary form in its increased energy content (which extra energy has been supplied to it by the electric discharge) and in the number of atoms contained in each molecule.

Although we know little about the number of atoms in the molecule of an element when in the solid state, it is probable that explanations similar to the above might be given for the allotropic modifications of sulphur and other elements besides oxygen.

NOTE—The student should now be able to calculate the volume of a gas evolved during any reaction.

The weight of a litre of hydrogen at N.T.P. is 0.0898 gram, or one gram of hydrogen measures 11.12 litres. We have already shown that the atomic weight of hydrogen is generally taken as unity, and we can therefore state that one atomic weight in grams of hydrogen measures 11.12 litres. If now another gas is  $n$  times denser than hydrogen, then 11.12 litres of that gas will weigh  $n$  grams. But as  $n$  is the density of the gas,  $2n$  is its molecular weight, and  $2n$  grams will measure 22.24 litres. So, uniformly, a molecular weight in grams of any gas measures 22.24 litres.

In the reaction represented by the equation



we see that one atomic weight in grams of copper reacts with two molecular weights in grams of sulphuric acid and yields one gram-molecule of sulphur dioxide. This we may write down at once as measuring 22.24 litres at N.T.P. We may calculate from this the volume of gas evolved with any other weight of copper or sulphuric acid at N.T.P. and then make any necessary corrections for temperature and pressure.

## CHAPTER XI

### ASHES

WHEN animal or vegetable matter is burned in air, the residue left is known as "Ash." The quantity and composition of this ash depends to a large extent upon the nature of the substance burned. Bones, for instance, yield nearly ten times as much ash as wood, and the ashes are composed of very different materials. Both of these substances—wood ashes and bone ash—are of great importance in the arts and in agriculture.

**Wood Ashes.**—When timber is felled the twigs and small boughs are cut off and are often burned. Formerly, this operation was carried out in iron pots to facilitate the collection of the ashes, and the product was therefore called "pot ashes." Nowadays, both in Canada and in the United States, where the process is still carried on, it is usually done in pits dug in the ground, but the name remains.

Wood ashes contain from 5 to 10 per cent. of potassium carbonate, which can be separated almost completely from the other constituents by solution in water. The product obtained on crystallisation, and which is called potash, contains 50 to 60 per cent. of potassium carbonate. By a further process of solution and recrystallisation a still purer substance containing upwards of 90 per cent. of potassium carbonate can be obtained. This is called "pearl ash" or "American ashes."<sup>1</sup>

<sup>1</sup> Potassium carbonate is chiefly obtained from potassium chloride, which occurs in the Stassfurt salt deposits as sylvite, KCl, and as carnallite, KCl, MgCl<sub>2</sub>·6H<sub>2</sub>O. The potassium chloride is heated with water, carbon dioxide, and magnesium carbonate under pressure—



The potassium magnesium salt is decomposed by heating with water to 120°,

**Potassium Carbonate.**—This substance closely resembles ordinary washing soda in its chemical properties. Its composition is represented by the formula  $K_2CO_3$ . It is usually sold as an anhydrous powder, but crystals of the formula  $K_2CO_3 \cdot 3H_2O$  can be formed from solution in water, in which it is readily soluble. Although a normal salt, its solution exhibits a strongly alkaline reaction. Like other carbonates, it reacts with all the common acids, forming the corresponding potassium salt, carbon dioxide and water. Practically all the other potassium salts can be prepared from it in this way, and it was formerly the chief source from which they were obtained. Since the discovery of enormous deposits of potassium salts—chiefly chloride and sulphate—at Stassfurt in Germany, the potassium carbonate obtained from wood ashes is not so largely employed.

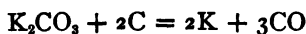
Potassium carbonate reacts with calcium hydroxide, forming potassium hydroxide (caustic potash). The reaction is similar to that for the preparation of caustic soda (p. 82).

A large number of potassium salts are used in the industries and in medicine. They closely resemble the corresponding sodium salts. The most important are the sulphate and the nitrate. Potassium sulphate occurs in the Stassfurt salt deposits as schönite,  $MgSO_4 \cdot K_2SO_4 \cdot 6H_2O$ , and as kainite,  $K_2SO_4 \cdot MgSO_4 \cdot MgCl_2 \cdot 6H_2O$ , from both of which it is extracted and is used as a potash manure. Kainite is also used for the same purpose, but the material supplied to the agriculturist under this name seldom or ever has exactly the composition represented by the formula given above. Potassium nitrate (p. 136) is used largely as the chief constituent in black gunpowder. Sodium nitrate cannot be used for this purpose, although it is cheaper, and the precipitated  $MgCO_3$  removed by filtering.  $KH \cdot Mg(CO_3)_2$  is potassium magnesium bicarbonate; compare "temporary hardness" (p. 70). Potassium carbonate is also obtained from "suint," a fatty material which forms a large percentage of the weight of sheep's wool, and from which it can be obtained by washing.

Root crops take up large quantities of potash from the soil; this is notably the case with sugar-beet. The molasses left after crystallisation of the sugar therefore contains considerable quantities of the potassium salts of organic acids. From these potassium carbonate is obtained by ignition. This forms another important source of the potassium compounds, as the sugar-beet is very widely cultivated in Europe.

because it absorbs moisture from the air and becomes damp. The nitrate is put into gunpowder to supply the necessary oxygen.

The metal potassium is obtained by strongly heating potassium carbonate with carbon in closed vessels, when the free element distils over—



Special precautions must be observed in this operation to prevent the formation of a compound of potassium with the carbon monoxide  $\text{K}_2(\text{CO})_6$ , which is highly explosive. An improved method of obtaining potassium consists of heating potassium hydroxide with carbon in the form of iron carbide, made by heating pitch with iron filings. No carbon monoxide is formed—

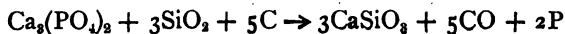


Potassium, a bright grey metal, is softer and less dense than sodium, and is even more readily oxidised.

**Bone Ash.**—When bones are burned the ash which remains amounts to something like half the weight of the original substance. It is insoluble in water but dissolves readily in dilute hydrochloric acid, and can be separated from the combustible matter in this way before the bones are burnt. The ash is in fact the incombustible mineral material which the bones contain. The combustible matter which remains after this “decalcifying” retains the colour, shape, and appearance of the bone, but is found to be soft and flexible. This shows that the rigidity of bones is due to the presence of the ash constituents.

It can be shown in various ways that bone ash consists mainly of phosphate of lime. Magnesium compounds and fluorine also enter into the composition of the ash, but they are present in insignificant quantities, and for the present, may be ignored.

When bone ash is mixed with carbon and silica and heated in closed retorts in an electric furnace, phosphorus distils over and may be collected under water—



**Phosphorus.**—Prepared as above, phosphorus<sup>1</sup> is a pale yellow, soft, wax-like solid (sp. gr. 1·83). It melts at 44° C., a temperature much below that of boiling water, and can be cast into any desired shape. For convenience, it is generally sold in the form of sticks of about one-third of an inch in diameter. It is intensely poisonous; even the fumes, when inhaled, give rise to a painful disease, necrosis of the jawbone, popularly called among match workers, who are most liable to contract it, “phossy-jaw.” The liability to the disease has, however, materially decreased with the more frequent use of red phosphorus in the preparation of matches. The temperature of ignition of yellow phosphorus (35°–45° C.) is much lower than that of sulphur and other common combustibles; in fact, phosphorus vapour will take fire even when mixed with steam. It therefore takes fire very readily in the air and must, for this reason, be handled with great care. The wounds inflicted by burning phosphorus are extremely painful. It is insoluble in water, and for safety is invariably kept immersed in it. Yellow phosphorus dissolves readily in carbon bisulphide (p. 84). When the solvent evaporates, the phosphorus separates in the form of crystals. If a small quantity of the solution in carbon bisulphide be poured on a piece of filter paper and allowed to dry, the phosphorus is left in a very finely divided condition, and takes fire spontaneously.

Other modifications of phosphorus are known. The most important is the red or amorphous variety. It is dark chocolate red in colour, it cannot be melted, but can be turned into vapour by heating, which on being condensed yields the yellow variety. When pure it is not poisonous. It is insoluble in carbon bisulphide and cannot be crystallised. Red phosphorus does not readily take fire, and may be safely kept uncovered.<sup>2</sup>

Yellow phosphorus changes into the red modification when

<sup>1</sup> Gk. *φῶς*, light; *φέρω*, I bear. It is called phosphorus because it appears luminous in the dark.

<sup>2</sup> Red phosphorus is familiar as the “striking part” on boxes of so-called safety matches.

heated to about 250° C. The change is accompanied by considerable evolution of heat (*i.e.* the phosphorus loses energy); it is greatly accelerated by the presence of a trace of iodine. The effect of the addition of iodine is complicated by the formation of an iodide of phosphorus. It is clear from the above that the red variety contains much less energy than the yellow, and this sufficiently accounts for its comparative inactivity.

**Phosphoric Anhydride.**—When any modification of phosphorus is burned in excess of air, it combines with oxygen and the oxide  $P_2O_5$  is formed. The substance appears in the form of dense white fumes (p. 16), which soon settle on the sides of the vessel as a white powder. It is called phosphorus pentoxide to distinguish it from other known oxides of phosphorus, all of which contain a smaller proportion of oxygen. It is often called phosphoric acid by farmers and others, but this name is wrong and is apt to prove misleading. The true relationship of the pentoxide to phosphoric acid, properly so called, is indicated by the name phosphoric anhydride (p. 87), which is often applied to it.

**Phosphoric Acid.**—The oxide  $P_2O_5$  is highly deliquescent. Its solution in water is accompanied by the evolution of a large amount of heat. This shows that the two substances enter into chemical combination forming a hydroxide just as lime does. Calcium oxide forms only one definite hydroxide, but phosphorus pentoxide can unite with water in three different proportions. On evaporating a solution just after it is made, a glassy mass is left which is known as metaphosphoric<sup>1</sup> acid. Its formula is  $HPO_3$ ,



If the solution be allowed to stand for several days and then evaporated the compound obtained has the composition  $H_3PO_4$ ,



This is known as orthophosphoric<sup>2</sup> acid. The third

<sup>1</sup> Gk. *μετὰ*, besides, among, etc.

<sup>2</sup> Gk. *ὀρθός*, right, true, correct, genuine, etc.



compound,  $\text{H}_4\text{P}_2\text{O}_7$ , known as pyrophosphoric<sup>1</sup> acid, is obtained by heating orthophosphoric acid for some time at a temperature of  $255^\circ\text{C}$ . when it loses water—



If the pyro acid is dissolved, it slowly recombines with the water it has lost and again forms orthophosphoric acid, but further heating of the pyro acid causes further loss of water and formation of the meta acid—



Phosphorus pentoxide is therefore an acidic oxide. Of the three acids which it forms with water, the ortho acid is by far the most important and its salts the commonest.<sup>2</sup> All the phosphates which occur in nature, e.g. bone-ash, coprolite, etc., are orthophosphates.

**Orthophosphates.**—When solutions of orthophosphoric acid are neutralised with sodium hydroxide, two of the three atoms of hydrogen in the acid are replaced by sodium. The composition of the salt is represented by the formula  $\text{Na}_2\text{HPO}_4$ , and it is called di-sodium hydrogen orthophosphate, or more generally common or neutral sodium phosphate.<sup>3</sup> If only one-half the quantity of sodium hydrate is used, only one of the three atoms of hydrogen is replaced by sodium. The salt formed is sodium di-hydrogen orthophosphate,  $\text{NaH}_2\text{PO}_4$  (acid sodium phosphate). It exhibits an acid reaction in solution in water. If orthophosphoric acid be mixed with sodium hydroxide to the extent of half as much again as is required to form the neutral phosphate, all the three hydrogens are replaced and the normal sodium salt can be formed. It is strongly alkaline and not stable in solution. The formula of the salt is of course  $\text{Na}_3\text{PO}_4$ .<sup>4</sup> As these three salts of soda can be formed from orthophosphoric acid we say that the acid is tribasic.

<sup>1</sup> Gk. *πῦρ*, fire.

<sup>2</sup> The three acids must be regarded as different kinds of phosphoric acid because they are all formed from the same acidic oxide.

<sup>3</sup>  $\text{Na}_2\text{HPO}_4$  shows a faintly alkaline reaction.

<sup>4</sup> As a rule, normal salts of all but feeble acids are neutral.

The corresponding salts of other bases can be prepared in a similar manner. The primary, secondary, and normal phosphates of potassium are represented respectively by the formulæ  $\text{KH}_2\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ , and  $\text{K}_3\text{PO}_4$ . The primary and secondary ammonium orthophosphates are well known. They are  $(\text{NH}_4)\text{H}_2\text{PO}_4$  and  $(\text{NH}_4)_2\text{HPO}_4$ . The tertiary or normal salt has not been prepared.

An important salt of orthophosphoric acid is obtained by adding a solution of ammonium chloride to one of ordinary sodium phosphate—



$\text{Na}(\text{NH}_4)\text{HPO}_4$  is then precipitated as crystals with four molecules of water of crystallisation. It is known as "Micro-cosmic Salt."<sup>1</sup> It is neutral to litmus.

The phosphates of the alkalies and of ammonium are soluble in water. The orthophosphates of the diad bases (Ca, Mg, etc.), except the primary salts, are insoluble. They are easily prepared, but owing to the difference in the valency of the bases, their formulæ are slightly more complex. The diad elements are so called because each atom replaces two atoms of hydrogen. In order to construct formulæ for the orthophosphates of the diads, therefore, it is simpler to take  $2\text{H}_2\text{PO}_4$ , which is equal, quantitatively, to  $\text{H}_6(\text{PO}_4)_2$ .<sup>2</sup> If two atoms of hydrogen in this are replaced by one atom of calcium, we obtain the formula  $\text{CaH}_4(\text{PO}_4)_2$  for the monocalcic orthophosphate, the calcium salt corresponding to the primary (acid) sodium orthophosphate<sup>3</sup>  $\text{NaH}_2(\text{PO}_4)$ . If all six atoms of hydrogen were replaced by three atoms of calcium, we should obtain the formula  $\text{Ca}_3(\text{PO}_4)_2$  for the normal or tricalcic orthophosphate, corresponding to the normal or trisodium phosphate. The formula for the intermediate compound corresponding to the secondary or di-sodium orthophosphate ( $\text{Na}_2\text{HPO}_4$ ) might be derived by substituting two atoms of

<sup>1</sup> Gk. *μικρος*, little; *κόσμος*, the world, universe, order, etc.

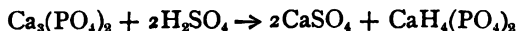
<sup>2</sup> It is not correct to express the formula in this way, though it is convenient to do so now for purposes of explanation.

<sup>3</sup> This might also be written—though incorrectly—as  $\text{Na}_2\text{H}_4(\text{PO}_4)_2$  to exhibit the analogy between the two compounds.

calcium for four atoms of hydrogen. This gives  $\text{Ca}_3\text{H}_2(\text{PO}_4)_2$ . It is, however, easily obtained from the ordinary formula for phosphoric acid  $\text{H}_3\text{PO}_4$  by substituting one atom of calcium for two atoms of hydrogen, and is generally written  $\text{CaHPO}_4$ .

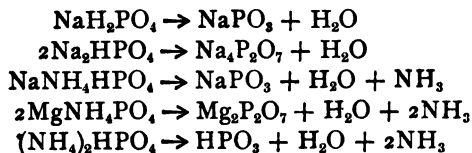
Several salts are known which contain both diad and monad bases in the same molecule. One of these, magnesium ammonium phosphate, obtained when magnesium chloride is added to the solution of a phosphate, in presence of ammonium salts and ammonia, is of special importance. It is represented by the formula  $\text{MgNH}_4\text{PO}_4$ .<sup>1</sup>

Phosphoric acid in a soluble form is essential for the growth of plants, and in order to supply it to an exhausted soil bone ash is sometimes used, but it is insoluble and its action is therefore slow. By treatment with sulphuric acid, however, the primary calcium phosphate is formed—



and this salt is soluble in water. The mixture of calcium sulphate and soluble calcium phosphate is largely used as a fertiliser. It is sold under the name of "Superphosphate of lime."

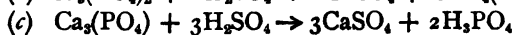
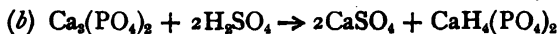
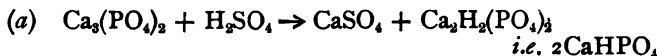
**Effects of Heat on Orthophosphates.**—The normal salts undergo no change on heating. When any orthophosphate which contains hydrogen atoms or ammonium is heated, the hydrogen atoms are expelled in combination with oxygen, as water, and the ammonium is volatilised as ammonia gas. Remembering this, it is easy to see what is left in each case. A few examples will make this plain.



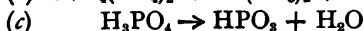
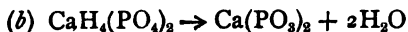
It is now possible to return to the preparation of the element phosphorus and explain the reactions by which it is obtained.

<sup>1</sup> It is of importance in the quantitative estimation of phosphoric acid.

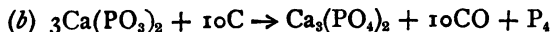
Bone ash and coprolite consist essentially of tricalcic phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ . This compound undergoes no change when heated, either alone or with charcoal. When acted upon by sulphuric acid, the calcium atoms may be successively withdrawn according to the equations—



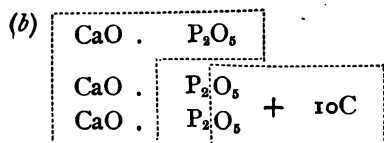
The substances obtained in reactions (b) and (c) can be used for the preparation of phosphorus. Both monocalcic phosphate and orthophosphoric acid lose water when heated strongly—



forming, respectively, calcium metaphosphate and metaphosphoric acid. If either of these substances be heated with carbon, it is reduced and free phosphorus is liberated and distils over—

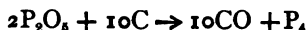


The action may perhaps be better understood if we remember that metaphosphoric acid is  $\text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ , and that orthophosphoric acid is  $\text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ . It is obvious that the corresponding calcium salts may be considered as  $\text{CaO} \cdot \text{P}_2\text{O}_5$  and  $3\text{CaO} \cdot \text{P}_2\text{O}_5$  respectively. The changes can then be represented in diagrammatic fashion as follows:—



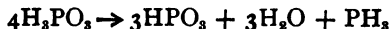
The action which takes place in the method for the preparation of phosphorus given on page 97 should now be intelligible; looking on  $\text{Ca}_3(\text{PO}_4)_2$  as equivalent to  $3\text{CaO}$ ,

$P_2O_5$ , the silica, which is an acidic oxide, has combined with the calcium oxide,  $CaO + SiO_2 \rightarrow CaSiO_3$ , and the liberated phosphorus pentoxide has been reduced by the carbon. When phosphorus pentoxide itself is heated with carbon it undergoes reduction, and the phosphorus is liberated as shown in the equation—

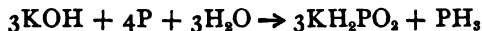


When phosphorus is oxidised in a limited supply of air the trioxide is formed. The vapour density of this compound shows that it must be represented by the formula  $P_4O_6$ . It combines with water forming phosphorous acid  $H_3PO_3$ . This acid, although it contains three atoms of hydrogen, is dibasic, only two of the hydrogen atoms being replaceable by a metal.

When phosphorous acid is heated it decomposes—



The compound  $PH_3$ , phosphine or phosphoretted hydrogen, is generally prepared by boiling phosphorus with a strong solution of caustic soda or potash—



The compound  $KH_2PO_2$  is the potassium salt of hypophosphorous acid  $H_2PO_2$ . This acid, although it contains three atoms of hydrogen, is monobasic. One of the hydrogen atoms only can be replaced.

Phosphine ( $PH_3$ ) is a colourless gas with a peculiar odour. It is insoluble in water and readily takes fire. In fact, the gas given off by the above reaction is spontaneously inflammable; this, however, is due to the presence of small quantities of another compound, liquid phosphoretted hydrogen,  $P_2H_4$ .

Phosphine can, under certain conditions, combine with  $HCl$ ,  $HBr$ , and  $HI$ , but at the ordinary temperature and pressure the compounds are not stable. They are  $PH_4Cl$ ,  $PH_4Br$ ,  $PH_4I$ , and are known as phosphonium chloride, bromide, and iodide respectively.<sup>1</sup>

<sup>1</sup> These compounds are of but little importance. The action of phosphine, however, in forming these compounds should be compared with that of ammonia (*q.v.* p. 127).

## CHAPTER XII

### SAND, CLAY, ETC.

"SAND" and "clay" are popular, not scientific, terms. They are not, therefore, capable of scientific definition. Any mass of small, gritty, angular fragments of minerals is popularly termed sand. The fragments may be all of one kind. More frequently the mass consists of several different kinds mixed together, but some particular mineral generally predominates.

Quartz is one of the commonest of rock-forming minerals, and as it is extremely hard and resistant to all kinds of chemical change, it usually forms a large proportion of any deposit of sand. Sea sand often consists almost exclusively of fragments of quartz.

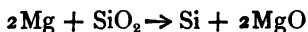
The only definite characteristic of sand is grittiness. This property which depends upon the size of the fragments would not generally be recognised in material consisting of particles greater than about  $\frac{1}{10}$  or less than  $\frac{1}{1000}$  of an inch in diameter. Material consisting of larger particles would generally be called gravel. When the particles are smaller than about  $\frac{1}{1000}$  part of an inch they are practically impalpable, and when moist cohere strongly together, forming a plastic mass which is commonly called "clay."

Occasionally the term "pure clay" is used to signify purified kaolin (china clay),  $H_4Al_2Si_2O_9$ , and similarly the term "pure sand" to mean quartz particles,  $SiO_2$ . But in view of what has been said above it is obvious that the words "sand" and "clay" should not be used with reference to the chemical nature of the substances, but only—if at all—with reference to the size of the particles.

Most of the rock-forming minerals are silicates, and, although insoluble, they are slowly acted upon by water, carbon dioxide, etc. When finely pulverised, they undergo chemical change relatively quickly, forming soluble compounds and colloidal hydrates. The latter are generally, but not necessarily, present in clay in considerable quantities and tend to increase its plasticity.

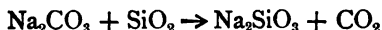
The crystalline mineral, quartz, is the oxide of an element known as silicon.<sup>1</sup> It has the composition  $\text{SiO}_2$  and is often called silica.<sup>2</sup>

Silicon is, next to oxygen, the most plentiful element in the crust of the earth. It may be obtained by the reduction of the oxide with metallic magnesium—



A certain amount of magnesium silicide,  $\text{Mg}_2\text{Si}$ , is formed at the same time. The oxide can also be reduced by carbon in the electric furnace. The free element is, however, of but little importance.

When the oxide  $\text{SiO}_2$  is fused with sodium carbonate, it displaces the carbon dioxide and forms a compound called sodium silicate—



Sodium silicate is soluble in water. It is the substance commonly sold under the name of water glass.<sup>3</sup>

When hydrochloric acid is added to a dilute solution of sodium silicate, silicic acid is precipitated as a whitish semi-transparent jelly. If, however, a dilute solution of sodium silicate is added to hydrochloric acid the silicic acid is not

<sup>1</sup> From Latin *silex*, flint. Flint is a mixture of crystalline and amorphous silica.

<sup>2</sup> Quartz is extensively used for spectacle lenses. It is peculiarly opaque to heat rays, but highly transparent to the so-called "actinic" rays (ultra-violet). It is also used for making test-tubes, flasks, and other chemical apparatus. Such quartz vessels can be plunged into water when red hot without cracking.

<sup>3</sup> A solution in water is used as an egg preservative. The eggs are dipped in the solution; when dry, they become covered with an air-tight coating of the silicate.

thrown down.<sup>1</sup> It can be separated from the sodium chloride formed, and from the excess of hydrochloric acid, by a process known as *dialysis*.

The solution is placed in a vessel similar to A, as shown in the figure, which is then suspended in water. The bottom of the vessel A is made of parchment. After some days it will be found that the whole of the sodium chloride and hydrochloric acid have passed into the water in the larger vessel, while nothing but silicic acid in solution remains in A. Substances which thus refuse to pass through a parchment membrane are non-crystalline, gluey materials. They have been called colloids.<sup>2</sup> Other substances will pass through such a membrane. Hence, the process of separation.

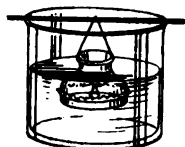


FIG. 14.

A colloidal solution differs from an ordinary solution in several ways. It freezes and boils at practically the same temperatures as the pure solvent (p. 116). It can be shown, in fact, that the substance is simply suspended in the "solvent," although in far too fine a state of division to be visible, or separated by ordinary filtration. Other insoluble substances may be obtained in the form of colloidal "solutions"; such are ferric hydroxide, alumina, and even certain metals, such as gold and silver.

The silicic acid present in the colloidal "solution" is thought to be orthosilicic acid,  $\text{H}_4\text{SiO}_4$ . On evaporation to dryness, an amorphous glassy mass is left which only partially dissolves in water, but neither this nor the precipitated silicic acid corresponds to the formula  $\text{H}_2\text{SiO}_4$ . Further heating drives off all the water, and silicon dioxide,  $\text{SiO}_2$ , is left.

The formula of the acid corresponding to the salt  $\text{Na}_2\text{SiO}_3$  is of course  $\text{H}_2\text{SiO}_3$ , and, by careful evaporation, the colloid "solution," obtained as above, could be evaporated till the

<sup>1</sup> On mixing strong solutions the gelatinous precipitate is always thrown down.

<sup>2</sup> Gk. *κόλλα*, glue.

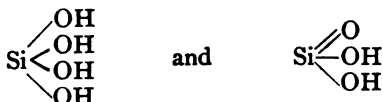


composition corresponded to that formula ; but this compound cannot be separated.

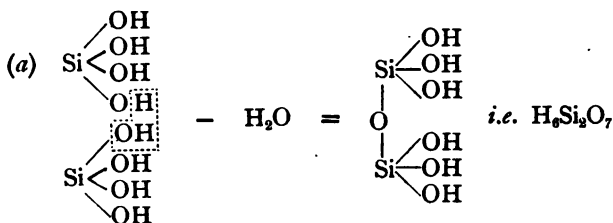
The rock-forming minerals apparently include salts of several silicic acids. A very few correspond to the hypothetical acid  $\text{H}_2\text{SiO}_3$ . Estatite and Wollastonite are examples, the formulæ of the pure substances being  $\text{MgSiO}_3$ ,<sup>1</sup> and  $\text{CaSiO}_3$ .<sup>1</sup>

Olivine<sup>2</sup> is also a silicate of magnesium, but the composition of the mineral is represented by the formula  $\text{Mg}_2\text{SiO}_4$ . This corresponds to the hypothetical orthosilicic acid previously mentioned.

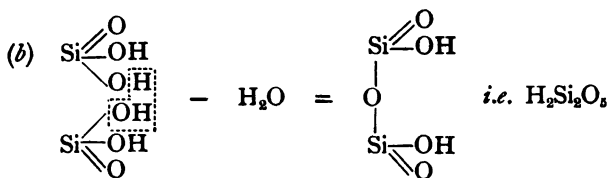
The formulæ for ortho- and meta- silicic acids can be represented thus—



It has been suggested that by the withdrawal of one molecule of water from two molecules of each of these acids, two disilicic acids can be formed—



Orthosilicic acid.

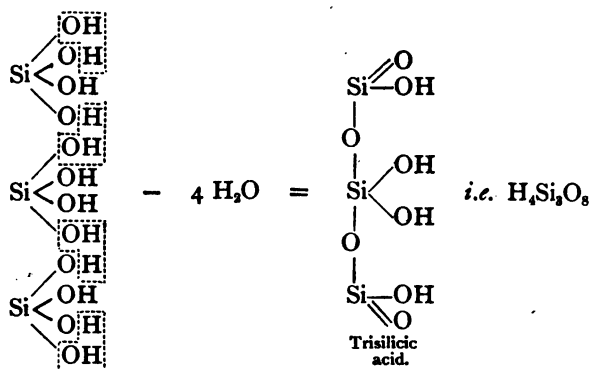


Metadisilicic acid.

<sup>1</sup> These, at any rate, are their simplest formulæ.

<sup>2</sup> Olivine is used in jewellery under the name of "peridot."

Also that by the extraction of four molecules of water from three molecules of the ortho acid a trisilicic acid is formed—



These formulæ afford a fairly simple explanation of the composition of some of the naturally occurring siliceous minerals, though many of them are too complex to be explained in this way; some probably contain more than one type of silicic acid, and others are probably acid or basic salts.

The following are some of the commoner silicates occurring in nature:

(1) Mica<sup>1</sup> (Muscovite),  $\text{K.H}_3\text{Al}_3(\text{SiO}_4)_3$ . This could be formed from three molecules of orthosilicic acid.

(2) Kaolinite,<sup>2</sup>  $\text{H}_2\text{Al}_2(\text{SiO}_4)_2.\text{H}_2\text{O}$ . A hydrated silicate of aluminium; it could be formed from two molecules of the orthosilicic acid.

(3) Felspar (orthoclase),  $\text{K.AlSi}_3\text{O}_8$ . Probably a trisilicate.

(4) Serpentine,  $\text{Mg}_3\text{Si}_4\text{O}_{10}.\text{H}_2\text{O}$ . Probably an orthodisilicate.

(5) Meerschaum,  $\text{Mg}_2\text{H}_4\text{Si}_3\text{O}_{10}$ . Probably  $\text{Mg}_2\text{Si}_3\text{O}_8.2\text{H}_2\text{O}$ , hydrated magnesium trisilicate.

(6) Asbestos. This is really a technical term; most of the

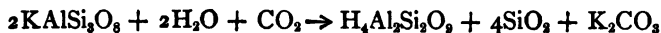
<sup>1</sup> Distinguished by its perfect cleavage. It is largely used for lamp chimneys and electric insulation.

<sup>2</sup> Kaolinite was considered to be present invariably as the chief substance in kaolin, or china clay. It is now thought probable that other hydrated silicates of aluminium may take its place.

material known in trade as "asbestos" is the fibrous variety of serpentine.<sup>1</sup>

(7) Talc,  $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ . This material when powdered forms what is known as "French chalk."

Kaolin<sup>2</sup> is formed during the weathering of granite rocks, owing to the action of carbon dioxide and water upon the felspar.



This is, however, not the only mode of production; besides felspar many other siliceous minerals, poor in magnesium, give kaolin under the action of the atmosphere. As the above equation shows, kaolin generally contains free silica (amorphous and hydrated), and often also particles of quartz. It is found mixed with compounds of iron, calcium, and magnesium, when it forms brick earth, pipeclay, etc. These are largely used in the making of bricks, tiles, and various kinds of coarse pottery, while the purer kaolin or china clay forms the chief material in the manufacture of porcelain.<sup>3</sup>

All kinds of clay form a stiff plastic mass with water, which can be moulded into any required shape. When dried it shrinks considerably, and on being strongly heated (fired) it shrinks still further, and forms an almost infusible mass which is not attacked by water or acids, and which can no longer be made into a paste with water. It is in this way that bricks, pottery, and porcelain are made. The presence of iron in the clay causes the red colour of the burnt material, as seen in brick, in many forms of common pottery, and in terra-cotta.

As burnt clay is very porous, pottery of all kinds is generally glazed.<sup>4</sup> For this purpose salt is thrown into the oven in which the pottery is being fired. The steam which the clay

<sup>1</sup> Owing to the fibrous nature of "asbestos" it can be woven into cloth or felted; its infusibility and poor conductivity for heat cause it to be used for packing steam tubes and incombustible fabrics.

<sup>2</sup> Kaolin is the Chinese name for the material. The words kao-ling are said to mean "high ridge" and to be the name of a hill where the clay was found.

<sup>3</sup> For making porcelain, pure kaolin is mixed with finely powdered quartz and felspar.

<sup>4</sup> China and porcelain, before glazing, is technically known as "biscuit."

gives off hydrolyses the salt, giving NaOH and HCl, and the alkali combines with some of the silica forming a fusible silicate, which melts and on cooling covers the pottery or brick with a hard glassy film. Red lead is also used for glazing. This causes the formation of lead silicate. For porcelain, the unglazed material is covered with a thin cream of powdered felspar and water, dried and heated to a white heat. The felspar melts and penetrates the porcelain in all directions, forming a thoroughly adherent glaze.

**Glass.**—This is essentially a mixture of calcium silicate with silicates of potash or soda. It is made by heating together sodium carbonate, powdered limestone and quartz sand. The composition of the product is approximately represented by the formula  $\text{CaO} \cdot \text{Na}_2\text{O} \cdot 6\text{SiO}_2$ . Glasses, however, vary greatly in composition; sometimes oxides of heavy metals, particularly that of lead, are added to the glass, while all coloured glasses contain silicates of other metals, such as iron, cobalt, and copper. Molten glass has, moreover, the power of forming a colloidal "solution" of certain of the metals, notably gold and copper, both of which impart a deep ruby tint to it. Many varieties of glass also contain borates.

Glass is almost unacted upon by acids; it is, however, appreciably attacked by pure water, and alkalis corrode it very considerably.

**Ultramarine.**—This is a deep blue material used as a pigment, for laundry blue, etc. It is now prepared by heating together kaolin, sodium carbonate, sulphur, and charcoal. The composition approximates to the formula  $\text{Na}_2\text{S}_3 \cdot 4\text{NaAlSiO}_4$ . The cause of the colour is, however, unknown.

Formerly it was prepared by powdering the natural blue mineral "lapiz-lazuli," which has a similar composition.

**Carborundum.**—This compound of silicon is of great value for grinding and polishing. It is made by heating together in an electric furnace, quartz sand and coke, with common salt—



As the formula (SiC) shows, the compound is carbide of silicon. It forms dark, almost black crystals, and is often

sold as a black glittering powder. When perfectly pure it is colourless. It is almost as hard as diamond.

**Fluorine.**—The element silicon and its compounds are readily attacked by fluorine, and by hydrofluoric acid.

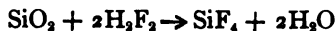
The element fluorine is found combined with calcium as fluor spar, the only fluorine mineral which occurs in really large quantities. It is calcium fluoride,<sup>1</sup>  $\text{CaF}_2$ . When this, or any other fluoride, is heated with sulphuric acid hydrofluoric acid is given off as a gas—



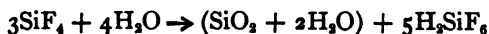
As hydrofluoric acid boils at  $19^\circ \text{C}$ ., it could be condensed in a suitable receiver. The anhydrous acid, however, has no industrial application, but the solution in water is largely used for etching glass. Owing to its powerful action upon siliceous material it cannot be kept in glass bottles, and vessels for containing it are made of gutta-percha, or sometimes of vegetable wax or paraffin wax, both of which resist the action of the acid.

Care must be taken in handling the acid. The gas is most irritating and dangerous. A strong solution in water produces painful wounds which are very difficult to heal.

The acid differs from the other halogen acids (p. 79), in that it is dibasic, and therefore two salts of potassium are known,  $\text{KHF}_2$  and  $\text{K}_2\text{F}_2$ . Its use for etching glass depends upon its action upon silica—



The compound  $\text{SiF}_4$ , silicon tetrafluoride, can be prepared by heating a mixture of sand or powdered glass, fluor spar, and concentrated sulphuric acid. It is a gas which is immediately decomposed on contact with water—



The silica, combined with water, perhaps as  $\text{H}_4\text{SiO}_4$  (orthosilicic acid), is precipitated and can be filtered off, leaving a solution of hydrofluosilicic acid.

<sup>1</sup> It is found largely in Derbyshire, and is hence known as "Derbyshire Spar," also, owing to its being often coloured bright violet, as "Blue John."

Fluorine<sup>1</sup> itself is a most active element and extremely difficult to obtain in a free state. It has been prepared by the electrolysis of anhydrous hydrofluoric acid, to which potassium hydrogen fluoride is added to impart electric conductivity. The preparation must be carried out in apparatus made of platinum<sup>2</sup> and fluor spar.

Fluorine combines with all the other elements except oxygen. It decomposes water immediately, liberating oxygen partly in the form of ozone (p. 93).

**Boron.**—This element is similar in many of its properties to silicon, although it is more closely related to aluminium, being always trivalent. It is, however, distinctly non-metallic in character, and its oxide is entirely acidic.

It occurs in nature combined with oxygen and hydrogen, or certain metals, as boric acid and its salts.

Boric acid is found in the "suffioni"<sup>3</sup> of Tuscany. The most important natural borate is borax,  $\text{Na}_2\text{B}_4\text{O}_7$ ,<sup>4</sup> the sodium salt of pyroboric acid.

Borax is soluble in water, and when in solution is decomposed by sulphuric or hydrochloric acid, boric acid<sup>5</sup> separating as flat pearly looking crystals.



Three boric acids are known. That having the composition  $\text{H}_3\text{BO}_3$  is called orthoboric acid, its salts are almost unknown. When heated to  $100^\circ \text{C}$ . it slowly loses water and is converted into metaboric acid  $\text{HBO}_2$ . Heating to  $140^\circ \text{C}$ . causes the formation of pyroboric acid (known also as tetraboric acid)—



<sup>1</sup> Lat. *fluo*, I flow. Fluorine derives its name from fluor spar. This mineral has been used for a long time as a flux in metal smelting, as it produces a fusible slag.

<sup>2</sup> Copper or lead is sometimes used, as these metals are soon covered with a protecting coating of fluoride.

<sup>3</sup> These are jets of steam issuing from the ground.

<sup>4</sup> The mineral sometimes known as "Tincal." Borax is generally sold as a crystalline material of the composition  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ . The hydrate  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  is also sometimes placed on the market.

<sup>5</sup> Boric acid is sometimes called boracic acid.

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Further heating drives off the whole of the water and leaves boric anhydride,  $B_2O_3$ , as a glassy mass.

As boric acid is a very feeble acid, a solution of borax is largely decomposed (hydrolysed) by water, so that it gives a strongly alkaline reaction, and when warmed with fats will saponify them (p. 165).

The presence of the acid can be detected by mixing the suspected substance with alcohol and sulphuric acid, and setting fire to the alcohol; the flame will be tinged green if boric acid be present.

Boric acid also colours turmeric paper brown.<sup>1</sup> If caustic soda be then added, the brown colour is changed to dark blue or black.

Boric acid and other mixtures of boric acid and borates are largely used as antiseptics and food preservatives.<sup>2</sup>

Borax melts when strongly heated, forming a clear transparent glassy material, and when molten has the power of dissolving various metallic oxides, which impart to it characteristic colours.

When hydrogen peroxide (p. 59) is added to borax in the presence of excess of caustic soda, sodium perborate,  $NaBO_3 \cdot 4H_2O$ , crystallises from the solution. It is soluble in water, but on warming decomposes with evolution of oxygen. It is extensively used as a bleaching agent in laundries.

## APPENDIX TO CHAPTER XII

**Osmotic Pressure.**—The phenomena due to osmotic pressure are connected with the process of dialysis described in the foregoing chapter.

All solutions are capable of exerting osmotic pressure, and the

<sup>1</sup> Alkalies also turn turmeric paper brown, but in this case caustic soda of course causes no further change.

<sup>2</sup> In using food preservatives, it should be noted that, in addition to any other physiological effect the preservative may have as a drug, its presence will always tend to impede digestion. It may be necessary sometimes to employ a preservative, and boric acid seems to be one of the least harmful. It has been suggested that cream might safely contain 0.25 per cent. and margarine and butter 0.5 per cent. of boric acid. On no account should any preservative be present in food for young children.

result is a tendency on the part of the solution to attract more of the solvent, and so, to expand.

If we take a glass tube, close it at one end with a piece of membrane such as ordinary bladder, and after having poured into it a small quantity of a solution of common salt, place it upright in a vessel of water with the closed end immersed, the liquid in the tube will rise. Water passes through the membrane into the tube, and at the same time a small quantity of salt passes in the opposite direction. If instead of using a piece of bladder, we employed a membrane, which, while allowing free passage of water, totally prevented the passage of the dissolved substance, the height to which the water would rise would be greater. Pzeffer in 1877 performed experiments with various membranes and found that the most effective was a freshly precipitated film of copper ferrocyanide. This is freely permeable for water, but practically impermeable for substances of high molecular weight, such as sugar. A membrane possessing such properties is said to be semi-permeable. A cell containing the copper ferrocyanide film can be prepared as follows: a porous (unglazed) earthenware jar is first placed under an air-pump and all the air removed from its pores; it is put into a dilute solution of copper sulphate, and filled with a dilute solution of potassium ferrocyanide. The liquids meet in the wall of the jar and produce by their interaction a precipitate of copper ferrocyanide. If the cell thus prepared be filled with a solution of cane sugar and put into a jar of pure water, water will pass through the cell wall into the sugar solution, but the sugar will not pass outwards. If when the cell is filled, it is closed, and fitted with a manometer, or instrument for measuring pressure, it will be found that the influx of water into the solution will cause a very remarkable increase of pressure. Thus a one per cent. solution of sugar at a temperature of  $15^{\circ}$  C. causes a pressure equal to about 540 millimetres of mercury, *i.e.* nearly three-quarters of an atmosphere. This pressure must be caused by the substance in solution, for if pure water be used, no such increase of internal pressure can be discovered.

This pressure is known as osmotic pressure, and it has been found to conform to the following laws. (a) It increases in proportion to the concentration; (b) It is proportional to the absolute temperature; (c) If two solutions give the same osmotic pressure their concentrations are proportional to the molecular weights of the substances dissolved. Comparison with the laws which state the connections between pressure, temperature, and volume in the case of gases (p. 11) shows that the laws of osmotic pressure are very similar; the first corresponds to Boyle's Law, the second to Charles's Law, and the third to Avogadro's hypothesis. In order to explain this remarkable connection, Van't Hoff has suggested that molecules of dissolved solids are in a condition similar to those of gases, and can therefore exert pressure on the vessel which contains them, as gases do, the solvent having little or no effect upon the result. This explanation is generally accepted.



To understand how this pressure might act, imagine a glass cylinder AC (Fig. 15), containing sugar solution and water, with a semi-permeable partition B between, as shown in the figure. As the molecules of sugar exert a pressure upon the under surface of the partition, they will tend to occupy a larger volume; but as they cannot pass through the partition, the only way in which the volume can increase is by water passing through into the sugar solution; this therefore takes place, and the partition moves up the cylinder.



FIG. 15.

An experiment of this nature can actually be performed. If instead of a sugar solution we take a concentrated solution of calcium nitrate, saturated with phenol (carbolic acid), and water also saturated with phenol,<sup>1</sup> separated by a thin layer—2 or 3 mm—of phenol, it will be found that this layer moves up the cylinder until it floats at the top. The phenol acts as a semi-permeable membrane, water passes freely through it, but calcium nitrate does not. The passage of a solvent through a membrane which is impermeable to the dissolved substance, caused, as has been shown, by osmotic pressure, is called *osmosis*.

If a dissolved substance passes freely through a membrane, it will, of course, produce no osmotic pressure; and when substances are separated by dialysis, those which pass through the membrane, are those which exhibit little or no osmotic pressure when that membrane is used. The measurement of the osmotic pressure of colloid solutions could be carried out with a parchment membrane, but this pressure is, in the case of such substances, very small indeed, owing to their excessively high molecular weight.

It will be seen that osmotic pressure tends to attract a solvent into the solution, and to retain it, and it therefore exerts a resistance to any process tending to remove the solvent. For this reason the boiling point of a liquid is raised when substances are dissolved in it, and the freezing point is lowered.

<sup>1</sup> The saturation of the two liquids with phenol, is to prevent the phenol layer from dissolving.

## CHAPTER XIII

### ORGANIC MATTER

THE chemical compounds which enter into the composition of plants and animals and their products, *e.g.* wood, humus, fat, flesh, wool, hair, bones, blood, milk, urine, dung, etc., differ in several important particulars from the common substances previously considered. They are more complex, *i.e.* the molecules of such compounds contain a larger number of atoms. When dried and heated in the air, they burn. The products of combustion are mainly gases, and are given off. The solid substances which remain are called ashes.

The combustible part is often called organic matter, *i.e.* the substance or product of an organism. The ash is, by contrast, often referred to as mineral matter. These names are, however, apt to prove misleading, because the ash is just as much an organic product as the combustible matter. The names, however, are in common use and must be accepted.

The chemical relation of the constituents of the ash—or some of them—to the compounds of which the combustible matter is made up is, in some cases, well known; in others it is very obscure.

All the compounds which enter into the composition of the combustible matter contain the elements carbon and hydrogen. The great majority also contain oxygen, and not a few contain nitrogen and sulphur as well.

When the substances are burned, the carbon, hydrogen, and sulphur combine with oxygen, forming oxides. Part of the oxygen is derived from the substance itself, and the remainder—the larger part—from the air in the presence of which combustion takes place. No oxide of nitrogen is

obtained, as nitrogen does not combine with oxygen at the temperature produced by the combustion. Nitrogen is, therefore, liberated in the free state.

**Destructive Distillation.**—When dry organic matter is heated in closed retorts it is charred, but not burned, because the air has no access to it. All the hydrogen, oxygen, and nitrogen, most of the sulphur and some of the carbon are expelled, but most of the carbon and some of the sulphur remain in the retort. The elements which are expelled by heat are not liberated in the free state, but as volatile compounds. These, when cooled, separate into three groups, viz. (1) tarry matter, (2) substances soluble in water, and (3) inflammable gases. The exact nature of each of these products depends, to some extent, upon the temperature and other conditions under which the operation is performed, and, in larger measure, upon the nature of the substance treated.

When wood or other vegetable matter is subjected to destructive distillation, the principal volatile products are water, acetone, wood spirit and pyroligneous acid. Wood spirit is one of the inflammable substances; it consists largely of methyl alcohol. Pyroligneous acid, when purified, is called acetic acid. The sour taste of vinegar is due to the presence of this compound, though vinegar is manufactured in a very different way. What remains in the retort is ordinary wood-charcoal. It consists of the free element carbon mixed with the ash ingredients of the wood. The latter can be separated by treatment with dilute acid, and pure carbon obtained. In the more ancient process of "charcoal burning," the pieces of wood were merely stacked on the ground, covered over with turves or clay to prevent free access of air, and set on fire. The heat evolved by the burning of part of the wood caused the remaining portion to be subjected to dry distillation, but all the volatile products escaped and were lost.<sup>1</sup> These volatile products are formed by the destruction of certain compounds during the process of distillation, and the innumerable minute

<sup>1</sup> This process is still carried on in Sweden, but special precautions are taken to collect the tar, which is sold as "wood-tar" or "Stockholm tar."

spaces which the compounds occupied in the original substance are left vacant. Charcoal is therefore, of necessity, an extremely porous substance, and has a large internal surface. When gases are brought into contact with solid surfaces they become denser and contract in volume; they are concentrated as a denser film at the common surface of the solid and gas. All porous substances, since they present a large extent of surface in small space, have, therefore, the power of absorbing gases in their pores. Charcoal exhibits this property in pre-eminent degree. That made from the denser kinds of wood has a larger number of smaller pores, *i.e.* a greater internal surface, and can absorb larger quantities of gas. Solid and liquid substances can also be removed from solution in water by charcoal in a similar manner.

This action is not to any large extent due to oxidation by any oxygen which may be present in the charcoal, as the efficiency of the charcoal is greater if it has been recently heated so as to expel all gas. It is dependent rather upon the fact that at the surface of contact between a solid body and a solution the dissolved substance becomes more concentrated than in the remaining part of the solution. Substances of complex composition may be removed from solution in this way. The phenomenon is sometimes known as *adsorption*. It is because of this action that drinking-water is often filtered through charcoal. Any complex organic materials present are adsorbed. Users of charcoal filters, however, should recognise that charcoal will not continue to remove organic matter indefinitely, and consequently frequent cleaning of the filter is necessary.

The power possessed by charcoal of absorbing gases can be illustrated by filling a tube with ammonia gas over mercury. If a piece of charcoal, preferably of some dense wood, and recently heated, be introduced, the mercury rises quickly, showing the absorption of the ammonia. Some kinds of charcoal absorb ninety times their own volume of ammonia gas; oxygen is absorbed to a much less extent; a dense charcoal only absorbs five times its own volume of this gas.

The effect upon colouring matter in solution is seen on mixing some litmus solution with powdered charcoal which

has been freshly heated. On filtering the mixture the liquid passes through the filter colourless.

Charcoal is used in sugar refining for the purpose of removing traces of brown resinous colouring material, and so giving a perfectly white sugar.<sup>1</sup> It has also the power of accelerating catalytically reactions between various gases, but in this respect it is far surpassed in efficiency by finely divided platinum.

Animal matter, such as bones, hoofs, horn, hair, wool, feathers, etc., contains a much larger proportion of nitrogen than wood and most other vegetable products, and when it is subjected to destructive distillation most of the nitrogen is given off in combination with hydrogen. This compound was long known as "spirit of hartshorn," but is now generally called ammonia.

Bone charcoal is often called animal charcoal, but the latter term properly includes charcoal made from blood, hides, etc.<sup>2</sup>

**Coal.**—Coal is often spoken of as a mineral because it is dug out of the ground. In reality, it is derived from vegetable matter, and was formed, perhaps, in a manner similar to that in which peat and other accumulations of a like nature are being formed at the present day. Marked differences have been observed in the composition of the upper and lower layers of peat deposits. The latter are always darker in colour and denser. They contain less hydrogen, oxygen, and nitrogen in proportion to carbon. It is by further changes of this kind, and strong compression due to the enormous weight of the superincumbent rock with which they have been covered up that such deposits have been converted into coal. Various "intermediate" products such as the German "brown coal"<sup>3</sup> are known. Similarly, anthracite or "stone coal" represents a further stage in the process by which ordinary soft or household coal is gradually transformed into graphite.

The last-mentioned substance is nearly pure carbon ; its

<sup>1</sup> The whiteness of refined sugar is generally increased by the addition of minute quantities of ultramarine.

<sup>2</sup> Bone charcoal is the material used in sugar refining.

<sup>3</sup> Known also as lignite. There are beds of it at Bovey Tracey in Devonshire.

formation is the final stage of the process by which all the gaseous elements are gradually eliminated. The hydrogen and oxygen of the original substance appear to be more rapidly dispersed than the nitrogen. At all events, ordinary coal contains less hydrogen and oxygen than wood does, while the nitrogen content is about the same,<sup>1</sup> or slightly greater.

Enormous quantities of coal are subjected to destructive distillation in order to obtain the inflammable gases which are used for illuminating and heating purposes. The process is carried out in fire-clay retorts, which somewhat resemble a long drain pipe in appearance. The form of carbon which remains is called coke. Owing chiefly to the greater density of the coal, coke differs in physical properties from other forms of charcoal. It is largely used for burning and also for various technical purposes, such as iron smelting.

The volatile products<sup>2</sup> of the dry distillation of coal consist of illuminating gas with various gaseous impurities, easily solidified hydrocarbons such as naphthalene, coal tar and ammonia. The mixture is passed through a cooling apparatus to condense the tarry material, and water in which the ammonia dissolves. The illuminating gas, which consists mainly of compounds of carbon and hydrogen, is insoluble in water. It is then passed over quicklime in order to dry

<sup>1</sup> The various materials mentioned can be compared in the following table, which gives their approximate percentage composition :—

	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
Cellulose	50	6	43	1
Peat	60	6	32	2
Lignite	67	5	25	2
Soft Coal	80	5	13	2
"	90	5	4	1
Anthracite	93	4	3	0

<sup>2</sup> Unpurified coal gas would probably contain the following constituents :—

Sulphuretted hydrogen	. . . . . 2	per cent.	} The percentages are subject to con- siderable varia- tions.
Carbon dioxide	. . . . . 2'5	"	
Unsaturated hydrocarbons	. . . . . 3	"	
Carbon monoxide	. . . . . 4'5	"	
Hydrogen	. . . . . 47	"	
Saturated hydrocarbons	. . . . . 38	"	
Nitrogen	. . . . . 3	"	

it and to remove the compounds of sulphur which it contains. When the lime is slaked and so contaminated with sulphur compounds that it will no longer act as a purifier, it is removed and sold as "gas lime." It is used to some extent by farmers.

The tar also consists mainly of compounds of carbon and hydrogen, and yields a great variety of useful products, such as benzene, carbolic acid, aniline, creosote, and bitumen or pitch.

The water containing the ammonia in solution is called the ammoniacal liquor. It is mixed with lime and distilled, and the ammonia which passes over is made to combine with sulphuric acid and thus form sulphate of ammonia. This substance is largely used as a nitrogenous fertiliser, and it is one of the most important sources of other ammonium compounds.

**Carbon.**—The element carbon is an essential constituent of every kind of organic matter. In most cases it can be obtained by destructive distillation, as described above. The solid black residue which remains—wood charcoal, bone charcoal, coke, etc.—when freed from ash and other impurities, is pure carbon. Fats, tar, and many other carbon compounds are not decomposed on heating, but in many cases, if burned in a limited supply of air, much of the carbon is separated as smoke, which, when collected, is called soot or lamp black—the latter is the soot from burning oil. All these forms of carbon are amorphous, and the differences in their physical properties are due merely to the accident of their mechanical condition.

Free carbon occurs in nature in two distinct crystalline forms.<sup>1</sup> The commoner of these is the familiar substance graphite, plumbago, or blacklead. The other form is the diamond. These two substances differ greatly in hardness, density, behaviour towards light, and other physical properties. Graphite is black, opaque, and so soft that it leaves a streak or mark when lightly rubbed on paper—hence its name graphite.<sup>2</sup>

<sup>1</sup> Substances occurring in two crystalline forms are said to be dimorphic (two formed).

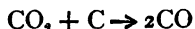
<sup>2</sup> Gk. *γράφω*, I write.

It has a specific gravity of 2.21. The diamond is transparent, and is of high refractive power towards light, *i.e.* rays of light entering the material obliquely are bent at the point of entry. It is the hardest of all known substances, and it is therefore used for cutting glass and for cutting and polishing other diamonds.<sup>1</sup> It has a specific gravity of 3.514.

Amorphous carbon can be crystallised. It dissolves in molten iron, silver, and other metals, and when these solutions are cooled much of the carbon separates in the crystalline form, but the crystals so obtained generally resemble graphite rather than diamond. If, however, the molten iron with its dissolved carbon be cooled by plunging in water, the outer part of the mass solidifies and contracts, thus subjecting the inner portion to immense pressure; under these conditions the carbon sometimes crystallises in the diamond form, but the crystals are very small.

The ultimate identity of all forms of carbon is established by their chemical properties. When heated in oxygen they all combine with it in the same proportion by weight, forming carbon dioxide (p. 68).

When carbon dioxide is passed over red-hot carbon it is reduced—



The compound produced is known as carbon monoxide. The equation given above is deduced from the fact that when the action takes place the volume of the gas is doubled—that is, every volume of carbon dioxide produces two volumes of carbon monoxide, and therefore every molecule of carbon dioxide gives two molecules of carbon monoxide.

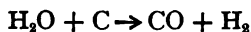
The reaction takes place in an ordinary coal fire, and its effects can be seen when all the hydrogen and other gases have been driven off and the residue of the coal is glowing. In these circumstances air enters at the bottom of the grate, and the coal there burns, forming carbon dioxide. This gas in passing over the red-hot coal in the middle and upper part

<sup>1</sup> The word “diamond” is from the Greek *ἀδάμας* (invincible), of which the words “adamant,” “diamant,” “diamond” are corruptions.



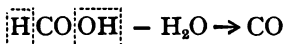
of the fire becomes reduced to carbon monoxide, which burns on passing into the air, with a blue flame.

Carbon monoxide is also produced when steam is passed over red-hot carbon. This is done in most gas-works, glowing coke being employed. The gas thus formed, is a mixture of hydrogen and carbon monoxide, and is known as water gas—

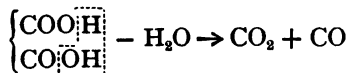


As water gas has no illuminating power it is generally enriched by mixing it with compounds of carbon and hydrogen, obtained by allowing a stream of high boiling rock-oil to fall while hot upon fire brick.

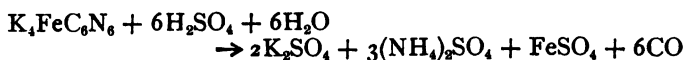
In the laboratory carbon monoxide is generally prepared by acting on certain carbon compounds with sulphuric acid. The most convenient is formic acid  $\text{H}.\text{COOH}$ . Concentrated sulphuric acid is employed, and it acts as a dehydrator, removing the elements of water but not otherwise taking part in the reaction—



Oxalic acid can be treated in the same way with similar results, but the carbon monoxide obtained is mixed with an equal volume of carbon dioxide, which can be removed by passing through caustic potash.



The gas is also readily prepared by heating potassium ferrocyanide with concentrated sulphuric acid—

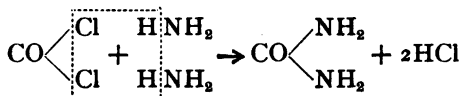


Carbon monoxide is a colourless gas, very slightly lighter than air, insoluble in water, and neutral to litmus. It is intensely poisonous; it forms a compound with the red colouring matter of the blood, which is difficult to decompose. Owing to the readiness with which it combines with more oxygen, it is a powerful reducing agent at high temperatures.

No salts corresponding to it are known, and it cannot therefore be regarded as acidic, but it forms remarkable compounds, known as carbonyls, with several of the metals, potassium (p. 97), iron, nickel,<sup>1</sup> etc.

It also combines readily with an equal volume of chlorine gas forming carbonyl chloride,  $\text{COCl}_2$  (phosgene gas).<sup>2</sup>

Carbonyl chloride reacts with ammonia—



The compound formed,  $\text{CO}(\text{NH}_2)_2$ , is known as carbamide, or urea; it is of great importance, and will be again referred to (p. 180).

**Ammonia.**—The principal nitrogenous compound obtained by the dry distillation of coal, bones, and other organic material containing nitrogen is called ammonia. It is a colourless gas, the specific gravity of which, compared with air, is 0.59; *i.e.* it is much less dense than air. It has a strong characteristic odour, can with moderate ease be condensed to the liquid state, and is readily soluble in cold water; one volume of water dissolves about 1150 volumes of ammonia at 0° C. The whole of the gas may be expelled from the solution by boiling. The concentrated solution has a specific gravity of 0.88 (water = 1).

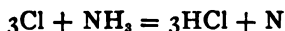
The composition of the gas corresponds to the formula  $\text{NH}_3$ . This is best proved in the following manner:—

A long tube (Fig. 16), closed at one end and fitted with a tap and funnel at the other, is filled with chlorine. A concentrated solution of ammonia is then allowed to run into the tube drop by drop. Vigorous action takes place, accompanied by flashes of light. When chemical action has ceased, the whole of the chlorine will have disappeared, and if water be allowed to run into the tube, it will continue to do so until it fills two-thirds of the length of the tube. The gas occupying

<sup>1</sup> Nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , forms the basis of a method for purifying the metal.

<sup>2</sup> Gk. *φῶς*, light; *γεννᾶω*, I produce.

the remaining one-third is found to be nitrogen, which must have come from the ammonia. The chlorine removes the hydrogen from the ammonia, forming hydrochloric acid, and sets the nitrogen free.



We started with three volumes of chlorine (the tube was full) and finished with one volume of nitrogen. But three volumes of chlorine will combine with three volumes of hydrogen, and as this hydrogen came from the ammonia gas, the one volume of nitrogen left, must, in the ammonia, have been combined with three volumes of hydrogen.

This, however, only gives the *proportion* by volume in which the two gases are present, and the formula might be not only  $\text{NH}_3$ , but  $\text{N}_2\text{H}_6$ ,  $\text{N}_3\text{H}_9$ , or any multiple of  $\text{NH}_3$ , for the proportion by volume would be the same in each case.

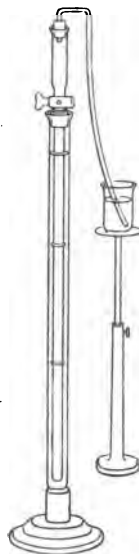
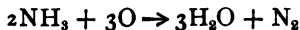


FIG. 16.

The density of the gas, however, is 8.5 compared with hydrogen, and therefore its molecular weight is 17 (p. 88). The atomic weight of nitrogen is 14, and the remainder, 3, is equal to the weight of 3 atoms of hydrogen. The formula is therefore  $\text{NH}_3$ .

When the dry gas is brought into contact with a flame it will burn, forming water and liberating nitrogen—



The combustibility of ammonia is, however, best shown by boiling a small quantity of a concentrated solution of the gas in a flask (Fig. 17), and at the same time passing in oxygen by means of a glass tube. On applying a light to the mouth of the flask the ammonia will burn with a yellow flame, and will continue burning if the supply of oxygen be properly adjusted.

Liquid anhydrous ammonia is without odour, and without action on litmus paper; the moist gas, however, and the solution are strongly alkaline.

When mixed with dry hydrochloric acid gas, ammonia gas forms dense white fumes, which settle on the sides of the vessel as a fine white powder. This substance is called ammonium

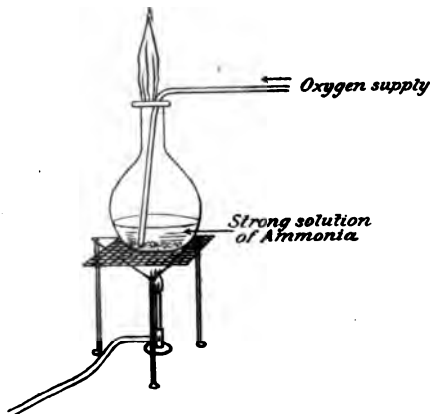


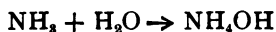
FIG. 17.

chloride, and is produced by the combination of the two gases—



Ammonium chloride was the first known compound of ammonia, and was called "Sal ammoniac"<sup>1</sup> (ammoniacal salt), a name which it still retains.

When ammonia gas dissolves in water a large amount of heat is evolved. This is partly due to the immense decrease in volume which the gas undergoes, and to a small extent to actual chemical combination with the water.

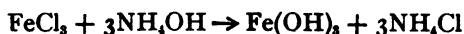


When ammonia is driven off from solution a like amount

<sup>1</sup> On the ancient trade route from Berenice (mod. Ben Ghazi) to the Nile was the Temple of Jupiter Ammon (the modern name for the place is Siwah). The surrounding oasis was a popular halting-place for caravans, and the chemical changes taking place in the immense amount of organic refuse which accumulated, led to the formation of ammonium chloride as an efflorescence on the soil. From the locality, and without any reference to its composition, the salt was called "Sal ammoniac," and when, much later, a gas was obtained from it, the gas was called ammonia.

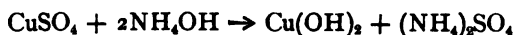
of heat must be absorbed. This may be shown by the following experiment. A flask about half full of strong ammonia solution is placed in a small pool of water on a board. Air is rapidly drawn through this solution by means of a filter pump, thereby removing the ammonia gas. The liquid is rapidly cooled, and ultimately the pool of water becomes converted into ice.<sup>1</sup>

That ammonia solution contains  $\text{NH}_4\text{OH}$ , ammonium hydroxide, is shown by its action upon solutions of the salts of many metals. When, for instance, it is added to a solution of ferric chloride, ferric hydroxide is thrown down—



That the solution also contains ammonia gas uncombined is shown by another action which often takes place.

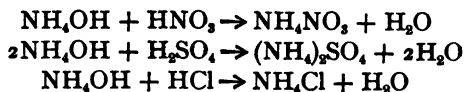
When, for example, ammonia solution is added to copper sulphate, at first a blue precipitate of copper hydroxide is thrown down—



but further addition of the solution of ammonia causes the precipitate to dissolve to a deep blue solution, from which a dark blue crystalline material separates out on addition of alcohol. This compound has the formula  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$ .

Many similar reactions are known.<sup>2</sup> Because of its action in precipitating hydroxides, the solution of ammonia gas is known as ammonium hydroxide. It exhibits the characteristic odour of the gas, and is strongly alkaline.

It can be neutralised by acids which act upon the ammonium hydroxide in much the same way as they act upon caustic soda or any other soluble hydroxide, *i.e.* they form water and the corresponding salt—



<sup>1</sup> Ammonia gas is used largely in the manufacture of ice. The gas is liquefied by pressure, and cooled. It is then allowed to freely evaporate, when great absorption of heat takes place.

<sup>2</sup> Silver chloride is soluble in ammonia solution, and a compound  $2\text{AgCl} \cdot 3\text{NH}_3$  can be separated.

These reactions, however, may be looked upon as direct unions of the ammonia with the acid, thus—



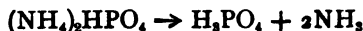
In all the salts formed, the group  $\text{NH}_4$  occurs, and this group plays the same part in the molecule as K or Na in the corresponding potassium or sodium compounds. The group  $\text{NH}_4$ , though it cannot be isolated, is called the radicle (*i.e.* root) of the compounds, and to it the name ammonium has been given. The metallic suffix "um" does not here suggest that ammonium is a metal, but rather that it so often takes that place in a molecule which is frequently occupied by a metal.

Owing to the fact that the basic radicle of the compounds is itself complex, ammonium salts are decomposed on heating. If the acid is a gas, such as hydrochloric acid, it is volatilised along with the ammonia, and the two recombine on cooling—

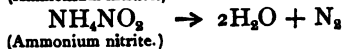
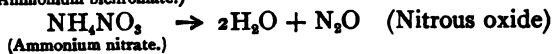
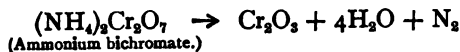


As the products of the decomposition do not automatically separate, but remain mixed at the higher temperature, we generally say the compound is dissociated. It is owing to this dissociation that ammonium chloride is volatilised by heat and sublimates on cooling.

If the acid is not volatile, the products of decomposition do not remain mixed and cannot, therefore, recombine on cooling. In other words, the ammonia is driven off and the acid remains—



If the acid is an oxidising agent, the hydrogen of the ammonia is oxidised—



From all its salts ammonia gas is displaced by the action of alkalis, and it is by this means that the gas is usually prepared—



Instead of caustic soda, lime or other basic oxides and hydrates may be used—



Similar reactions take place in solution; the ammonia gas dissolves in the water, but is expelled on boiling, and can be recognised by its odour.

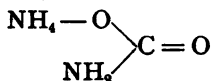
Other important salts of ammonia, besides those mentioned above, are the carbonate and sulphide.

The carbonate  $(\text{NH}_4)_2\text{CO}_3$  is very unstable and smells strongly of ammonia; the bicarbonate  $\text{NH}_4\text{HCO}_3$  can be formed by treating ammonium hydroxide with excess of carbon dioxide.

Ammonium "sesquicarbonate" is the sublimate obtained by heating a mixture of ammonium chloride and powdered chalk ( $\text{CaCO}_3$ ). It is a mixture of bicarbonate and ammonium carbamate. The carbamate is also formed when dry ammonia and dry carbon dioxide are mixed together—



It is a substance closely related to urea (p. 180), and can be represented graphically—



Ammonium sulphide is used in chemical analysis. The solution is prepared by passing sulphuretted hydrogen into ammonium hydroxide, and contains both  $\text{NH}_4\text{HS}$  and  $(\text{NH}_4)_2\text{S}$ . It decomposes on keeping, depositing sulphur, and becoming yellow from the formation of other ammonium sulphides.

**Putrefaction and Decay.**—When organic matter putrefies, the compounds of which it consists are gradually broken down and various compounds of hydrogen are produced. The simplest of these compounds are Marsh gas ( $\text{CH}_4$ ), water, sulphuretted hydrogen, and ammonia, and these being gases are given off. It will be seen that this change is in some respects analogous

<sup>1</sup> These equations suggest the use of ammonium chloride, but of course any other salt of ammonium could be employed.

to that produced by destructive distillation, and though it takes place more slowly, the products are to some extent the same. Putrefaction, like destructive distillation, can only take place in the absence of air, because, in both cases, the products are fairly easily oxidised, and therefore would not otherwise be obtained.

In the presence of air, destructive distillation gives place to combustion, and putrefaction changes to decay, which is slow oxidation. The final products of decay are oxides instead of hydrides—



Both putrefaction and decay are caused by bacteria, and a certain degree of moisture and warmth are necessary for their action. Within certain limits the greater the warmth and amount of moisture the more rapidly do the bacteria act and the more rapidly are the changes accomplished.

The oxides  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{N}_2\text{O}_5$  are all acidic, and tend to inhibit the action of the bacteria which cause decay. The process, therefore, soon comes to an end unless lime or some other basic oxide is present to combine with these products and form neutral salts—carbonates, sulphates, and nitrates.

The process of decay takes place naturally in soils, and is called, by agricultural chemists, nitrification. It is in this way that the organic matter of the soil—the roots of previous crops and the manure applied to the land—is changed into humus, and that the nitrogen and other constituents finally become available as plant foods. In soils that are very tightly packed and waterlogged, nitrification is arrested and putrefaction set up, because air does not readily find access to such soils. The products of putrefaction are more or less poisonous to vegetation.

The process of nitrification is sometimes promoted by artificial means. For this purpose the organic matter is mixed with earth and lime and so made into what farmers call a compost. The heap is then well watered with liquid manure, which contains plenty of bacteria, and covered over to protect it from rain. The time required to complete the change depends



largely upon the temperature. When it is complete, the material is carted out and spread upon the land.

This method was formerly employed for the production of nitrates which were used for making gunpowder, and other purposes. The material, instead of being spread on the land, was lixiviated with water, and the nitrates, being soluble, dissolved. To convert the calcium nitrate into potassium nitrate (saltpetre) it was only necessary to add potassium carbonate to the solution. The calcium carbonate produced by double decomposition is insoluble, and can therefore be separated by filtration. The soluble potassium nitrate can be obtained from the solution by crystallisation.

Artificial composts are not now required for the production of nitrates, because about a hundred years ago large deposits of nitrate of soda were discovered in Chili. This in its crude form is known as caliche; it was probably formed from organic matter by a natural process of nitrification, and the deposits have been preserved because the region in which they are found is practically rainless.

**Fixation of Atmospheric Nitrogen.**—As nitrogen is of such great importance to plants, and the growth of grain is absolutely necessary for the support of human life, various attempts have been made to utilise atmospheric nitrogen, which, as has been already stated, plants cannot assimilate while it is in the free state (p. 21). Several methods are now in use.

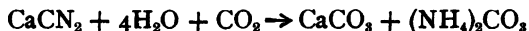
It was shown in a previous chapter (p. 21) that small quantities of oxide of nitrogen are formed by the direct combination of oxygen and nitrogen which takes place under the influence of electric discharges. It has long been known that this process could be imitated on the lecture table. With the enormous development of electrical science which has taken place in the last few years, it has been found possible to carry it out on a large scale, and nitrates are now commercially manufactured by the Birkland and Eyde process in this way. Instead of a small spark, a very powerful current is employed, and the gases (*i.e.* air) are passed through what is described as "a roaring disc of flame." Under these conditions the oxygen and nitrogen combine and the oxide of nitrogen so produced

is brought into contact with lime or other bases, and the corresponding nitrates are formed.

The oxide formed when oxygen and nitrogen thus unite is nitrogen peroxide, which in contact with water gives nitric acid and nitric oxide, NO. The nitric oxide readily takes up further oxygen, forming a further quantity of nitrogen peroxide.

The manufacture of nitrates by this method is developing rapidly, and it seems probable that it will be employed not only for producing nitrates for agriculture, but also for other purposes. At present nitric acid and the compounds derived from it are chiefly prepared from the nitrate of soda imported from Chili.

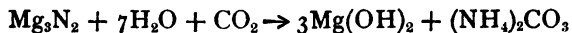
A second method for the "fixation" of atmospheric nitrogen also depends upon the application of electric energy. When nitrogen is passed over calcium carbide (p. 159) in an electric furnace, it combines with the carbide, forming a compound known as calcium cyanamide  $\text{Ca.C.N}_2$ —or,  $\text{Ca} = \text{N} - \text{C} \equiv \text{N}$ . This substance is also used as a nitrogenous fertiliser, as in the soil the nitrogen it contains is converted into ammonium carbonate and finally into nitrate—



The following are also important :—

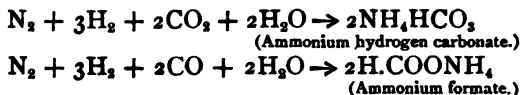
(1) *The Production of Nitrides of Silicon or Magnesium.*—

When magnesium oxide is mixed with coal or coke, heated in an electric furnace and nitrogen gas is passed through the mixture, the oxide is reduced and the liberated metal unites with the nitrogen forming magnesium-nitride ( $\text{Mg}_3\text{N}_2$ ). This substance is readily acted on by acids—even carbonic acid—with the formation of the corresponding ammonium salt, thus—

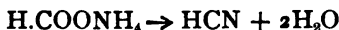


Silicon nitride behaves in a similar manner. These compounds might be used as nitrogenous manures; but, though the oxides are cheap enough, the cost of manufacture of the nitrides is at present prohibitive.

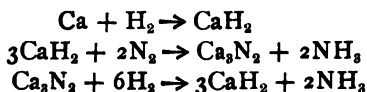
(2) *The Synthesis of Ammonia*.—Air and steam are passed over white hot coke and the mixture of gases thus obtained (p. 24) is then passed over wood charcoal, spongy platinum or other catalyser. They are then mixed with more steam and again passed through the same apparatus. The reactions which take place may be represented by the following equations—



Ammonium formate exhibits a tendency to decompose into hydrocyanic acid and water—



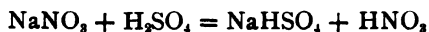
Ammonia is formed also when a mixture of nitrogen and hydrogen is passed over heated metallic calcium. In this case, the hydride  $\text{CaH}_2$  is first formed and ammonia is ultimately produced from it by the reactions expressed in the following equations—



Nitrogen combines directly with hydrogen to a certain extent when an electric spark is passed through a mixture of the gases.

(3) *Formation of Cyanides*.—When a mixture of carbon and potassium carbonate is heated to bright redness and nitrogen gas (air) is led over the glowing mass, the nitrogen enters into combination and forms potassium cyanide KCN. This is one of the oldest, and until comparatively recent years, it was almost the only known method of causing the free element nitrogen to enter into combination.

**Nitric Acid**.—When nitrate of soda, or any other nitrate, is heated with concentrated sulphuric acid, nitric acid distils over. This change may be represented by the equation—



It has been argued from this that sulphuric acid is the stronger acid, *i.e.* that it has a greater affinity for bases than nitric acid. The inference, however, is not strictly accurate. More heat is evolved in the formation of nitrates than in the formation of the corresponding sulphates, and that is a more accurate measure of chemical affinity.<sup>1</sup>

The action of sulphuric acid on nitrates does not proceed very fast or very far unless the nitric acid is removed (by distillation) as it is produced. Otherwise, there is a tendency for the reverse change to take place, and a condition of equilibrium, which is determined by the relative masses of the reacting bodies, is set up.

Nitric acid is a liquid, sp. gr. 1.53. When pure it is colourless, and has a strong characteristic odour. Generally nitric acid is coloured yellow by the presence of nitrogen peroxide.

The composition of nitric acid is indicated by the formula  $\text{HNO}_3$ . As the name of the substance implies, it has strongly acid properties; it turns blue litmus red, decomposes carbonates, and combines with basic oxides to form well-defined salts (nitrates).

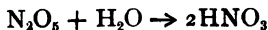
In concentrated solution it is an oxidiser, and, with certain organic compounds, it forms nitro-compounds, *i.e.* it introduces, into these compounds the group  $\text{NO}_2$ , most of which are yellow in colour. For this latter reason it stains the skin yellow.

Its oxidising power is well seen in its action upon carbon which is caused to deflagrate, and also upon tin—



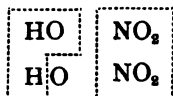
As the equation shows, the acid is itself reduced.

It is easy to understand this and other similar reactions if we remember that nitric acid is a hydrate, *i.e.* a compound of  $\text{N}_2\text{O}_5$  with water—



<sup>1</sup> Moreover, when equivalent quantities of  $\text{NaOH}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  mutually react in dilute aqueous solution, two-thirds of the soda combines with the nitric acid and one-third with the sulphuric acid. Nitric acid in aqueous solution is therefore a "stronger" acid than sulphuric acid.

The formula for nitric acid can be written  $\text{HO}\cdot\text{NO}_2$ , and the change which takes place in it when it acts upon tin can be indicated as follows :—



When nitric acid acts upon copper, the change which takes place depends upon the strength of the acid employed. With a somewhat diluted acid nitric oxide is produced—



But if concentrated acid be employed, nitrogen peroxide is obtained—



The fact that the acid is acting as an oxidising agent is seen from the liberation of oxides of nitrogen, which in each case contain less oxygen than is present in the nitric acid, *i.e.* less than in  $\text{N}_2\text{O}_5$ .

Nitric acid acts upon silver, lead, and other metals in a similar manner. Dilute nitric acid has less effect upon these metals, but upon zinc, iron, and other easily oxidisable metals it acts vigorously, forming nitrates and liberating oxides of nitrogen, nitrogen, or ammonia. The nature of the products depends upon the temperature and concentration of the acid.

With very dilute nitric acid, magnesium causes the evolution of hydrogen; a fact which is of some importance as it emphasises the acidic properties of nitric acid when it is made very dilute.

All nitrates are soluble in water. When heated strongly in the dry state they undergo decomposition.

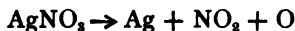
The nitrates of the alkali metals (p. 193) lose oxygen on being heated—



The nitrates of the heavy metals lose oxygen and nitrogen peroxide, and leave an oxide—



If the oxide is unstable the metal itself will be left—



Nitric acid (hydrogen nitrate) behaves like the nitrates of the heavy metals, *i.e.* it is split up into the oxide ( $\text{H}_2\text{O}$ ),  $\text{NO}_2$  and oxygen which may be collected.

Nitrate of ammonia decomposes completely (p. 129).

**The Oxides of Nitrogen.**—(1) *Nitrous Oxide*,  $\text{N}_2\text{O}$  formed by the decomposition of ammonium nitrate. It is a colourless gas, slightly soluble in cold water, neutral to litmus. When inhaled it produces in some people a form of hysteria, and is therefore called "laughing gas." If, however, it is breathed in a pure state it produces insensibility, and is therefore used by dentists as an anæsthetic. Combustible bodies such as sulphur will burn in it, combining with the oxygen and liberating nitrogen.

(2) *Nitric Oxide*  $\text{NO}$ .—Generally prepared by the action of slightly diluted nitric acid upon copper (p. 206). It is a colourless gas insoluble in water, and neutral to litmus. It rapidly takes up oxygen, forming nitrogen peroxide. It supports combustion in the same way as nitrous oxide does.

(3) *Nitrogen trioxide*,  $\text{N}_2\text{O}_3$ .—The reduction product of nitric acid formed when that acid is acted upon by starch or white arsenic  $\text{As}_2\text{O}_3$ . When condensed it forms a deep blue liquid. In the gaseous state it is almost entirely dissociated into  $\text{NO}$  and  $\text{NO}_2$ .

$\text{N}_2\text{O}_3$  is the anhydride of nitrous acid  $\text{HNO}_2$ , the salts of which are known as nitrites. The formation of potassium nitrite from the nitrate has already been mentioned.

Both nitrates and nitrites are sometimes found in natural waters, particularly surface water. Any water containing appreciable amounts of these compounds should, if it is to be used for domestic purposes, be viewed with suspicion; not because the nitrates and nitrites are themselves dangerous, but because they are formed, as has been shown, by the oxidation of organic matter almost always of animal origin. Organic matter may therefore be present in the water, and

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this may possibly be accompanied by bacteria of putrefaction and disease.

(4) *Nitrogen peroxide*,  $\text{NO}_2$ , the brown oxide of nitrogen, is soluble in water, with which it forms nitric acid and nitrous acid or nitric oxide.

(5) *Nitrogen pentoxide*,  $\text{N}_2\text{O}_5$ , the anhydride of nitric acid. It can be obtained from the acid by treatment with phosphorus pentoxide,  $\text{P}_2\text{O}_5$ —



It is a white solid very readily soluble in water. It speedily decomposes into nitrogen peroxide and oxygen with evolution of heat.

## CHAPTER XIV

### PARAFFINS AND THEIR DERIVATIVES

DURING the putrefaction of vegetable material in the presence of moisture various gaseous products are evolved. One of these is particularly noticeable as coming off in bubbles from the vegetable refuse which collects at the bottom of stagnant pools. If a glass jar be filled with water and inverted with the mouth below the surface of the pool and the mud below it stirred, it is possible to collect the gas in the jar.

Owing to its formation in the circumstances described, the gas is known as Marsh gas. If a lighted match be applied to the gas it will burn, forming carbon dioxide and water.

Marsh gas is also formed during the destructive distillation of organic matter and constitutes a large percentage of gas coal. It is also given off from coal in the mine, and is the "fire damp" of the coal-miner.

For experimental purposes marsh gas is generally prepared by heating dry sodium acetate with caustic soda or soda lime—



It is colourless, tasteless, odourless, and practically insoluble in water.

Analysis of the gas shows that it consists of carbon and hydrogen only, and its percentage composition and its density (eight compared with hydrogen) lead to the formula  $\text{CH}_4$ . In its general properties it closely resembles a large series of compounds of hydrogen and carbon which are known as the paraffins, and which are found in petroleum or rock oil. Many of these compounds are in general use as fuels under the names of paraffin oil, etc.



Ordinary paraffin oil is a familiar substance easily recognisable by its peculiar characteristic odour. It is a liquid, lighter than water and insoluble in it. It takes fire readily and burns with a brightly luminous flame.

It is obtained from the crude petroleum,<sup>1</sup> which springs from the earth in certain places on the shores of the Caspian Sea, in the United States of America and Canada. A similar material is obtained by destructive distillation of bituminous shales in Scotland.

All these products consist not of a single pure substance, but of a mixture of many which can be separated more or less completely by processes of distillation.

The crude petroleum contains marsh gas and other substances, gaseous at the ordinary temperature, but these are largely given off on exposure to the air. On distillation it is found that the petroleum has no definite boiling point, but that the temperature of ebullition gradually rises, and condensable vapours are given off at all temperatures. The most volatile products come over first, the liquid commencing to boil at about  $38^{\circ}\text{C}$ ., and the distillate which is condensed between this temperature and about  $100^{\circ}\text{C}$ . constitutes the extremely volatile material known as "petrol" or "motor spirit." When this is removed, liquids of higher boiling point are given off and condensed; these form the material known by various names such as benzoline, gasoline, etc. On continuing the heating, further products are obtained, most of which are used as lamp oils, and after these have been collected, further separation yields lubricating oils, vaseline, and solid paraffin (paraffin wax).

By careful redistillation, each of the liquid products can be separated into a number of more or less pure substances, but it is impossible by mere distillation to obtain each constituent compound in petroleum in a perfectly pure condition.

By special treatment, however, a liquid can be obtained with a constant boiling point of  $38^{\circ}\text{C}$ ., another with a constant

<sup>1</sup> Crude petroleum often contains sulphur compounds. These give an objectionable odour to the oil itself, and produce sulphur dioxide on burning. They are removed by heating the oil with copper oxide,  $\text{CuO}$ .

boiling point of  $70^{\circ}\text{C.}$ , a third which boils at  $98^{\circ}\text{C.}$ , and others which boil at  $125^{\circ}\text{C.}$ ,  $148^{\circ}\text{C.}$ , etc. Analysis and general study of these compounds have caused the formulæ:  $\text{C}_6\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_7\text{H}_{16}$ ,  $\text{C}_8\text{H}_{18}$ ,  $\text{C}_9\text{H}_{20}$  to be assigned to them respectively. Others which are gaseous at ordinary temperatures are represented by the formulæ:  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ .

It is obvious that a close relationship exists between these compounds. They are all hydrocarbons (*i.e.* compounds of hydrogen and carbon only), and, commencing with marsh gas  $\text{CH}_4$ , there is a complete series in which each member differs by one carbon atom and two hydrogen atoms from that immediately preceding it. In each case also the number of hydrogen atoms is just two more than twice the number of carbon atoms. To express this fact a general formula (*i.e.* one which applies to each compound) is used, it is  $\text{C}_n\text{H}_{2n+2}$ . Here if " $n$ " is 1, then  $2n + 2 = 4$ , and the hydrocarbon is  $\text{CH}_4$ . If " $n$ " is 6 then  $2n + 2 = 14$ , and the hydrocarbon is  $\text{C}_6\text{H}_{14}$ .

A series in which the members differ by a constant quantity is called a homologous series. The series now being considered is that of the *paraffin hydrocarbons*. Other homologous series are known.

A special nomenclature has been adopted for these compounds, and names given to them which, in most instances, indicate by the use of a Greek numeral the number of carbon atoms in the molecule, and which terminate in the syllable "ane."

Thus—

$\text{CH}_4$  is Methane.

$\text{C}_2\text{H}_6$  „ Ethane.

$\text{C}_3\text{H}_8$  „ Propane.

$\text{C}_4\text{H}_{10}$  „ Butane.

$\text{C}_5\text{H}_{12}$  „ Pentane.

(This marks the commencement of the use of the Greek numeral prefix.)

$\text{C}_6\text{H}_{14}$  is Hexane.

$\text{C}_7\text{H}_{16}$  „ Heptane.

$\text{C}_8\text{H}_{18}$  „ Octane.

$\text{C}_9\text{H}_{20}$  „ Nonane.

$\text{C}_{10}\text{H}_{22}$  „ Decane.

$\text{C}_{11}\text{H}_{24}$  „ Undecane.

$\text{C}_{12}\text{H}_{26}$  „ Dodecane,

etc., etc.

The first four members of the series are gases at ordinary

temperatures, the succeeding members from pentane to hecdecane  $C_{16}H_{34}$  are liquids, and the remainder solids. It will be seen that as the molecule increases in complexity<sup>1</sup> the higher the boiling point becomes, although there is not a regular difference between the boiling points of successive members of the series. The difference is less in the case of the higher members of the series than in the case of the lower.

Thus Pentane  $C_5H_{12}$  boils at  $38^\circ\text{C}.$ , and Hexane at  $70^\circ\text{C}.$ , a difference of  $32^\circ\text{C}.$ ; Octane boils at  $125^\circ\text{C}.$ , Nonane at  $148^\circ\text{C}.$ , a difference of  $23^\circ\text{C}.$

In chemical behaviour, the paraffin hydrocarbons are singularly inert; neither caustic soda, sulphuric acid, nor hydrochloric acid have any effect upon them. The name "paraffin" is intended to emphasise this point.<sup>2</sup>

**Fuels.**—Perhaps the most important application of the paraffins is as fuel. All fuels contain either hydrogen or carbon, or both, and their use depends upon the fact that these elements when combining with oxygen give out large amounts of heat.

Occasionally alcohol is used as a fuel, but this is not so effective as an equal weight of a hydrocarbon, since it already contains oxygen as well as hydrogen and carbon, and therefore less oxygen is necessary to convert it into carbon dioxide and water, and less energy in the form of heat is liberated. The use of liquid fuel is rapidly extending owing to its portability, cleanliness, and convenience in use.

**Lamp Oils.**—Oils for use in lamps should be free from the more volatile paraffins, as otherwise they will give off an inflammable vapour at ordinary temperatures. The temperature at which an oil gives off an inflammable vapour is called its flash-point. In Great Britain no oil, the flash-point of which is below  $73^\circ\text{F}.$ , can be sold as lamp oil. This is somewhat low, but nearly all specimens of lamp oil on sale in the country will be found to have their flash-points considerably higher.

<sup>1</sup> This statement applies strictly to the normal members of the series only. An important qualification will be found in more advanced works on organic chemistry.

<sup>2</sup> Lat. *parum, affinis*, lit. little affinity.

**Lubricating Oils.**—The use of some of the less volatile paraffins as lubricants depends upon the fact that they do not dry, and do not oxidise in the air; there is, therefore, no chance of their forming any acid substances which might corrode metal, or resinous material which might increase friction.

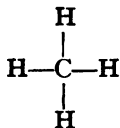
**Vaseline.**—This substance is also used as a lubricant. Its use in medicine arises from its being neither acid nor alkaline, from its permanency, in that it does not decompose or in any way change on keeping; also from its having the usual inert character of the paraffins, and not reacting with any of the medicaments with which it may be mixed.

**Paraffin Wax.**—This substance is soluble in paraffin oil, and in benzene, and solutions in one or other of these solvents are used for waterproofing leather (boots, etc.). A solution in turpentine is occasionally rubbed into wood to form a temporary protection against water and acids.

Paraffin wax is also largely used in the manufacture of candles. It occurs as a solid mineral occasionally, when it is known as "ozokerite."

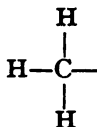
**Constitution.**—As methane is correctly represented by the formula  $\text{CH}_4$ , it is evident the carbon in it is tetravalent. By no known process can carbon be made to combine with more than four atoms of hydrogen or their equivalent, and therefore, before any other compound can be formed from methane, some of the hydrogen must be removed.

For instance, two molecules of methane cannot unite, but if one atom of hydrogen were removed from each, leaving  $\text{CH}_3$ , these residues might combine together. This can be represented graphically. Methane, for example, can be written—

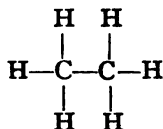


The *four* lines radiating from the carbon atom merely signify

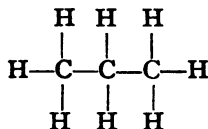
that carbon is tetravalent. The residue,  $\text{CH}_3$ , will then be represented as—



and two of these may readily join together—



forming a molecule of  $\text{C}_2\text{H}_6$ . It is plain that in this molecule the two carbon atoms must be directly united. This process might be repeated indefinitely, so that from  $\text{C}_2\text{H}_6$  a hydrogen atom might be removed and another  $\text{CH}_3$  added in its place, forming—



*i.e.*  $\text{C}_3\text{H}_8$ , and so the next compound  $\text{C}_4\text{H}_{10}$ , being  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$ .

As a matter of fact this kind of formula does completely represent the paraffin hydrocarbons, and is in general use. The formulæ show diagrammatically the following characteristics of the paraffins.

- (a) The number of hydrogen atoms is just two more than twice the number of carbon atoms.
- (b) Each member of the series differs by  $\text{CH}_2$  from that immediately preceding it.
- (c) Every atom of carbon is exercising its full combining power, and therefore no other compounds can be formed from the paraffins except by removal of hydrogen.<sup>1</sup>

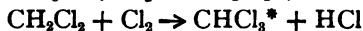
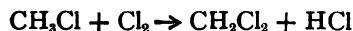
<sup>1</sup> It must be carefully noted that we do not assume the formulæ and deduce the properties of the paraffins from them. The formulæ are used as diagrammatic representations of facts obtained by experiment.

Compounds which exhibit this last property of forming other compounds only when certain of the elements they already contain are removed, are called *saturated* compounds, and the derivative compounds are said to be formed by *substitution*.

The paraffins are saturated hydrocarbons, for we find that only substitution compounds can be formed from them. As a simple example, consider what takes place when methane is mixed with chlorine. When the mixed gases are exposed to the action of sunlight, part of the chlorine enters into the methane molecule, in place of hydrogen, which is removed in combination with the rest of the chlorine. Thus,



This, however, may proceed further, until all the hydrogen has been replaced by chlorine—



These compounds, in which atoms of hydrogen are replaced by atoms of chlorine, are known as chlor-substitution products. It would be difficult to obtain the pure compounds by the method suggested.

Similar compounds can be derived from other paraffins, and we have thus three homologous series of such derivatives (omitting those in which the whole of the hydrogen is replaced), viz. the monochlor-substitution products of the general formula  $\text{C}_n\text{H}_{2n+1}\text{Cl}$ ; the dichlor-substitution products of the general formula  $\text{C}_n\text{H}_{2n}\text{Cl}_2$  and the trichlor-substitution products,  $\text{C}_n\text{H}_{2n-1}\text{Cl}_3$ .

When one hydrogen atom of methane is replaced by any other element, the group  $\text{CH}_3$  will be found in the substitution product. This group is referred to as methyl. Similarly, in the mono-substitution products of ethane, the group  $\text{C}_2\text{H}_5$  will

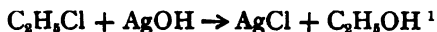
\*  $\text{CHCl}_3$  is the compound known as chloroform.

†  $\text{CCl}_4$ , Carbon tetrachloride. A volatile, inflammable liquid; both it and chloroform have well-marked anæsthetic properties.

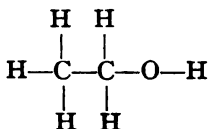
## 146 A FOUNDATION COURSE IN CHEMISTRY

be found; this is known as ethyl;  $C_3H_7$  is propyl,  $C_4H_9$  is butyl, and so on.

The compounds derived from ethane by substitution of the hydrogen by chlorine are  $C_2H_5Cl$ ,  $C_2H_4Cl_2$ ,  $C_2H_3Cl_3$ , etc. The first of these,  $C_2H_5Cl$ , may be called monochlorethane. It is, however, often referred to as ethyl chloride. It is a volatile liquid. It reacts, under proper conditions, with moist silver oxide, forming silver chloride, and a hydroxyl derivative of ethane, which we may call ethyl hydroxide—

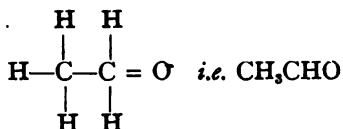


Ethyl hydroxide can be represented thus—



The formula shows diagrammatically that the chlorine has now been replaced by hydroxyl<sup>2</sup> (OH). Oxygen is a dyad element, and therefore the group OH is capable of combining with one more atom of hydrogen or any other monad element, or with one monad group, such as ethyl.

The two atoms of chlorine in dichlorethane  $C_2H_4Cl_2$  may be replaced by one atom of oxygen, giving—

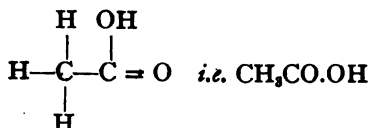


In the case of trichlorethane, both replacements are possible, *i.e.* one atom of chlorine by hydroxyl, and the other two atoms

<sup>1</sup> The corresponding iodine compound  $C_2H_5I$  being less volatile is much more convenient for this substitution.

<sup>2</sup> Whenever the group OH occurs in combination it is known as hydroxyl. It cannot, of course, be obtained free, any more than methyl or ethyl. These and others are complex radicles occurring only in combination.

of chlorine by oxygen. The formula of the resulting compound would be—



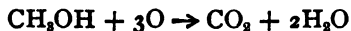
Monohydroxyl derivatives of the paraffin hydrocarbons are

called alcohols. Compounds containing the group  $\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array}$  are known as aldehydes, and those containing  $-\text{CO.OH}$  all possess acidic properties, and are known as organic acids.

Chlor-substitution compounds corresponding to those given above can be derived from all the paraffins, and there are three homologous series of oxygen compounds corresponding to them—

- (a) Alcohols of the general formula  $\text{C}_n\text{H}_{2n+1}\text{OH}$
- (b) Aldehydes   "       "       "        $\text{C}_n\text{H}_{2n}\text{O}$
- (c) Acids       "       "       "        $\text{C}_n\text{H}_{2n-1}\text{O.OH}$

**Alcohols.**— $\text{C}_n\text{H}_{2n+1}\text{OH}$ . Methyl hydroxide,  $\text{CH}_3\text{OH}$ , or methyl alcohol, the first member of this series, is the hydroxyl derivative of methane. It is produced in considerable quantity by the destructive distillation of wood and in the crude (unpurified) state is commonly called "wood spirit" (p. 118). Pure methyl alcohol is a colourless, volatile, neutral liquid. It has a faint characteristic odour and taste. It readily burns in the air, forming carbon dioxide and water <sup>1</sup>—



Ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) is the common alcohol, or "spirit of wine." It was to this substance that the name alcohol <sup>2</sup> was originally given, and the name was only extended to other members of the series because it was found that they all possess very similar properties and are all hydroxyl derivatives

<sup>1</sup> The complete combustion of compounds containing carbon and hydrogen always gives carbon dioxide and water.

<sup>2</sup> The name is of Arabic origin.



of hydrocarbons. It then became necessary, in order to distinguish the different kinds of alcohol, to add another word (methyl, ethyl, etc.), corresponding to the name of the hydrocarbon from which the particular alcohol is derived.<sup>1</sup>

Common (ethyl) alcohol is generally obtained by the fermentation of sugars, which occur naturally in the juice of fruits or are produced by a preliminary treatment, from starchy grains. The fermentation of sugars is caused by certain organisms like yeast, which are always found adhering to the outside of the fruit. When the fruit is crushed, the organisms become mixed with the juices and so cause the change by which the juice is converted into wine. In order to set up fermentation in the sugary liquor extracted from malt, it is necessary to add yeast, but the change takes place in much the same way.<sup>2</sup> The alcohol so produced may be separated from water, and other constituents of these fermented liquors by distillation. This is how it came to be called spirit of wine.<sup>3</sup>

The resemblance between pure ethyl and methyl alcohols is so close that it is very difficult to distinguish one from the other or to separate them. The chief difference is that methyl alcohol boils at about  $67^{\circ}$  C. and ethyl alcohol at  $78^{\circ}$  C. This of course is merely a particular case of the general rule that, in any homologous series, the members which contain a larger number of carbon atoms boil at a higher temperature.

Ethyl alcohol also burns with a non-luminous (and therefore non-smoky) flame. It is used as a fuel in the so-called "spirit-lamps." It is also used as a solvent for gums and resins in the manufacture of varnish, and in many other industrial processes.

<sup>1</sup> The term "alcohol" is therefore the name not of one substance but of a large class of substances.

<sup>2</sup> Further discussion as to the nature of fermentation will be found on p. 174.

<sup>3</sup> Although ethyl alcohol boils at  $78^{\circ}$  C. and water at  $100^{\circ}$  C., it is not possible to separate these liquids by distillation only, though a product containing about 96 per cent. of alcohol can be obtained in this way. To complete the drying, the distillate must be allowed to remain in contact with quick-lime for some time and then redistilled. The quick-lime combines with the water. The ordinary drying agents, calcium chloride and sulphuric acid, cannot be used, for both combine with the alcohol.

As a constituent of wine and other alcoholic beverages, it is subject to a very high duty. This tax is remitted when the alcohol is used for burning and for industrial purposes, provided that ten per cent. of crude wood spirit is added to it, so as to render it unfit for drinking purposes. This mixed product is called methylated spirit. A more recent enactment requires the addition of one per cent. of mineral naphtha to methylated spirit, but this requirement may be dispensed with in certain cases. The presence of the naphtha is shown on the addition of water, when a cloudiness is produced, owing to the fact that the water does not dissolve the mineral oil.

Propyl and butyl alcohols are respectively derived from propane and butane. They also resemble ethyl alcohol, but boil at higher temperatures according to the number of carbon atoms they contain.

**Aldehydes.**— $C_nH_{2n}O$ . The aldehydes, as has been pointed out, may be regarded as the oxygen derivatives of hydrocarbons, corresponding to the dichlor-substitution products. They are generally prepared by the gentle oxidation of alcohols, but may also be obtained by the reduction of acids (p. 152).

To prepare ethyl aldehyde,  $C_2H_4O$ , *i.e.*  $CH_3CHO$ , ethyl alcohol and sulphuric acid are added to a solution of potassium bichromate in a flask. The potassium bichromate acts as the oxidising agent, and the action generally commences without the application of heat. In any case very gentle warming is sufficient. The aldehyde which is formed is a volatile liquid, boiling at  $21^\circ C.$ , it has a characteristic fruity odour.

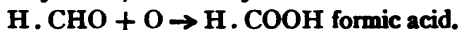
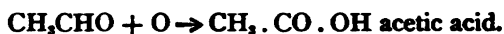


Methyl aldehyde  $CH_2O$ , *i.e.*  $H.CO.H$ , cannot be prepared from methyl alcohol in the same manner, but is formed when a mixture of the vapour of the alcohol and air is passed over a heated spiral of platinum wire. Both of these aldehydes are soluble in water and in alcohol in all proportions.

The aldehydes are powerful reducing agents. If an aqueous solution of an aldehyde and a few drops of ammonia be added to silver nitrate solution, on warming, metallic silver is

deposited.<sup>1</sup> If also to a solution of copper (cupric) sulphate, a drop or two of a solution of an aldehyde be added and then caustic soda, a red precipitate of cuprous oxide is thrown down on warming.

In these reducing actions, the aldehyde is oxidised forming an acid—



For this reason ethyl aldehyde and methyl aldehyde are generally referred to as acetic aldehyde and formic aldehyde, names which are sometimes further contracted into acetaldehyde and formaldehyde.

Formaldehyde has never been obtained in a pure condition, but a solution in water known as formalin is largely used as an antiseptic. It is used as a preservative for milk and other foods.

One of the chief properties of aldehydes is their power of combining with other substances. Thus, with hydrogen they form alcohols, with oxygen, acids. They also combine directly with ammonia, hydrocyanic acid, and with alkaline sulphites.

If acetic aldehyde be allowed to stand, it combines with itself, *i.e.* it undergoes condensation, forming more complex molecules, though the proportion between the elements remains the same. Thus, if a few drops of sulphuric acid be added to acetic aldehyde, the solution becomes hot, and on cooling to 0° C. crystallises. The substance formed is called paraldehyde, and its formula is  $\text{C}_6\text{H}_{12}\text{O}_6$ , *i.e.* 3 molecules of aldehyde united. Under other conditions another solid product is formed, known as metaldehyde. The formula of this is unknown, as it is not easily soluble in any solvent, and on vaporising, it is reconverted into aldehyde.<sup>2</sup> These

<sup>1</sup> Glass mirrors are sometimes made in this way.

<sup>2</sup> When a solution of acetaldehyde is warmed with strong caustic potash, the liquid becomes yellow, and an amorphous yellowish red precipitate separates after a short time. This is known as aldehyde resin. If, however, a very dilute caustic potash solution be employed (or sodium acetate, or zinc chloride) instead of strong caustic alkali, the aldehyde undergoes condensation and a substance is formed having the formula  $\text{C}_7\text{H}_8\text{O}_7$ . Now,

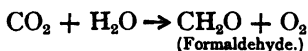
two compounds are said to be polymeric modifications of aldehyde.

The name "aldehyde" was given to these compounds because of their preparation from alcohol. The action of the oxidiser, potassium bichromate, may be indicated by the equation—



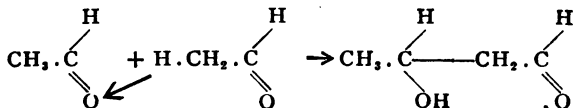
from which it will be seen that the action of the oxygen may be considered as taking two atoms of hydrogen from the alcohol molecule. The resulting compound was therefore first known by the "Latin" term (*al*)cohol (*dehyd*)rogenatum, *i.e.* alcohol dehydrogenated, a term which has been contracted as indicated by the brackets. By continuing the action of potassium bichromate, the aldehyde may be further oxidised to the corresponding acid.

Formic aldehyde may be looked upon as a simple member of a class of compounds known as carbohydrates (p. 170). These compounds contain carbon, hydrogen, and oxygen, the hydrogen and oxygen being present in the same proportions as in water. If the formula for formaldehyde be written  $\text{CH}_2\text{O}$ , the resemblance is obvious. Moreover, it has been shown that probably formaldehyde is formed in plants from the carbon dioxide and water vapour which they inhale through the stomata of their leaves. It is well known that the action of the plants in the presence of sunlight is to assimilate the carbon of the carbon dioxide and to liberate its oxygen. This is probably done according to the following equation—



It is quite possible that the formaldehyde thus formed may undergo a kind of condensation and form more complex

acetaldehyde is  $\text{C}_2\text{H}_4\text{O}$ , and therefore the substance formed is quantitatively equal to  $2(\text{C}_2\text{H}_4\text{O})$ . It is known as aldol, and its formation may be represented as follows :—



molecules (cp. paraldehyde). From the chemical point of view, the possibility is well established, for formaldehyde, by the action of lime water, undergoes condensation of this kind and forms a sweet, syrupy substance which is a mixture of compounds having the formula  $C_6H_{12}O_6$ <sup>1</sup> (equal quantitatively to  $6CH_2O$ ). It is known as formose. If an action similar to this takes place in plants, and a compound  $C_6H_{12}O_6$  be formed, starch might possibly be formed afterwards by the abstraction of water.

**Acids.**  $-C_nH_{2n-1}O.OH$  or  $C_nH_{2n+1}COOH$  or  $C_nH_{2n}O_2$

When alcohols or aldehydes are strongly oxidised, the two hydrogen atoms attached to the carbon which is already partly oxidised are replaced by oxygen, according to the equation—

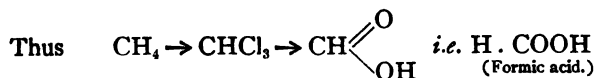


The compounds so produced turn blue litmus red, combine with bases to form salts with the liberation of water, and in general exhibit all the characteristic properties of acids.

The acids corresponding to the first few members of the series of paraffin hydrocarbons are—

- (1) Formic acid,  $HCOOH$ , from  $CH_4$ .
- (2) Acetic acid,  $CH_3COOH$ , from  $C_2H_6$ .
- (3) Propionic acid,  $C_2H_5COOH$ , from  $C_3H_8$ .
- (4) Butyric acid,  $C_3H_7COOH$ , from  $C_4H_{10}$ .

As before stated they may be considered as corresponding to the trichlor-substitution products of the hydrocarbons—

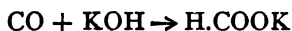


The first member of the series, formic acid, derives its name from the fact that it is found in the bodies of red ants.<sup>2</sup> It also occurs in stinging nettles (*Urtica dioica*); the pain of the sting is probably caused by the injection of a small amount

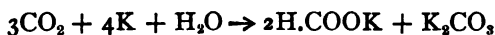
<sup>1</sup> Aldol condensation (p. 151, note).

<sup>2</sup> Latin, *formica*, an ant.

of formic acid secreted by the leaf of the plant. It can be formed from methyl alcohol by oxidation; also synthetically by submitting a mixture of carbon monoxide and steam, or carbon dioxide and hydrogen, to the action of the silent electric discharge. The salts of formic acid are known as formates. Potassium formate can be made by neutralising the acid with caustic potash or, in a more interesting manner, by the action of carbon monoxide upon strong caustic potash at  $100^{\circ}\text{C}$ .—

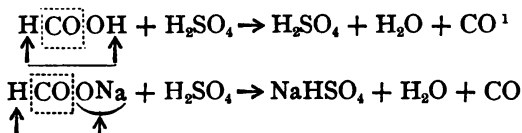


or again, by allowing moist carbon dioxide to act upon metallic potassium—



It is also formed from hydrocyanic acid (p. 179), but is generally prepared by distilling oxalic acid with glycerine.

Formic acid and formates evolve carbon monoxide when treated with sulphuric acid (p. 124)—



Acetic acid,  $\text{CH}_3\text{COOH}$ , the second member of the series, is derived by oxidation from ethyl alcohol. It is one of the products obtained in the destructive distillation of wood (p. 118). When weak wine is exposed to the air, it turns sour owing to the formation of acetic acid by oxidation of the alcohol. The change is promoted by the action of certain micro organisms, and is in fact a kind of fermentation.<sup>2</sup> The product was called vinegar, but in this country the liquid commonly sold under that name is now manufactured by acetic fermentation of other alcoholic liquors.

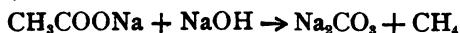
<sup>1</sup> Compare this decomposition with the synthesis of formic acid from carbon monoxide and water and of formates from carbon monoxide and caustic alkali.

<sup>2</sup> The organism chiefly employed in acetic acid fermentation is that known as "mycoderma aceti" (Gk. *μύκης*, a mushroom or fungus; *δερμα*, skin), or bacterium aceti.

The production of vinegar<sup>1</sup> is carried on by allowing dilute alcohol (wine, beer, etc.) to drop upon shavings which have been first steeped in vinegar to provide the micro organism. The shavings have the effect of distributing the alcohol over a large surface and so quickening the oxidation of the alcohol. Commercial acetic acid is generally made by the distillation of wood.

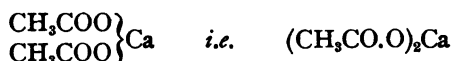
When pure, the acid is a colourless liquid, which becomes solid at a temperature of  $16.6^{\circ}$  C. In this state it much resembles ice in appearance, and is therefore called glacial acetic acid.

- The salts of acetic acid are known as acetates, that of sodium is  $\text{CH}_3\text{COONa}$ . When the acetates of the alkalis are heated strongly with caustic soda or lime, they yield marsh gas (p. 139)—



All the acids of this series are monobasic (p. 57). No matter how many hydrogen atoms they contain, only the hydrogen of the hydroxyl group can be replaced by a metal. (In the acids whose formulæ are given on page 152, the hydrogen which is replaceable is underlined.)

The formula for the acetate of a monad element such as sodium is therefore  $\text{CH}_3\text{CO.ONa}$ , for a diad element—



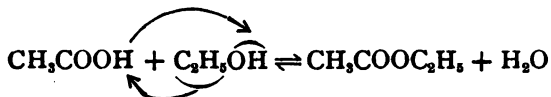
the corresponding butyrates would be  $\text{C}_3\text{H}_7\text{COONa}$  and  $(\text{C}_3\text{H}_7\text{CO.O})_2\text{Ca}$ .

**Esters.**—The formula for ethyl alcohol is always written  $\text{CH}_3\text{CH}_2\text{OH}$  or  $\text{C}_2\text{H}_5\text{OH}$  (not  $\text{C}_2\text{H}_6\text{O}$ ), because the substance exhibits many of the characteristic properties of a hydroxide. As a matter of fact it is often called ethyl hydroxide. Like ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) it, and the other alcohols, can form compounds with acids, which can be looked upon as salts. Thus we have ethyl acetate, ethyl sulphate, ethyl butyrate, and so on. Such compounds of the alcohols with acids are called ethereal salts or, more shortly, esters. The

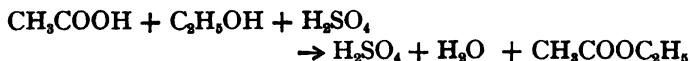
<sup>1</sup> Acetic acid derives its name from the Latin, *acētum* = vinegar.

method of preparation of these esters can be illustrated by that of ethyl acetate.

The equation representing the reaction may be written—



The ester is not satisfactorily prepared by merely mixing the alcohol and the acid, for, as the equation represents, the action is reversible, and not only does acetic acid act upon alcohol giving ethyl acetate and water, but water reacts with ethyl acetate, giving again the acid and the alcohol. A condition of equilibrium is therefore reached in which the two reactions just balance one another, unless something is put into the mixture to remove the water which is produced. The material generally employed is concentrated sulphuric acid, and if a mixture of acetic acid (or sodium acetate), alcohol, and concentrated sulphuric acid be distilled, ethyl acetate can be collected, as, owing to the presence of the sulphuric acid and the consequent removal of the water, the reaction only proceeds in one direction, and will go on to completion—



The method given may be taken as typical of that employed in the general production of esters.

The alcohols have not the strongly basic properties of ammonium hydroxide, or of most of the metallic hydroxides, and the ethereal salts are not stable like the salts of ammonium and of metals, as is shown by their easy decomposition with water.

Many esters similar to ethyl acetate occur in nature, and many are made and sold as "fruit essences." Thus ethyl butyrate,  $\text{C}_3\text{H}_7\text{COOC}_2\text{H}_5$ , is known as essence of pineapple, while amyl<sup>1</sup> acetate,  $\text{CH}_3\text{COOC}_5\text{H}_{11}$ , is sold as essence of Jargonelle pear.

<sup>1</sup> Amyl alcohols are those of the formula  $\text{C}_5\text{H}_{11}\text{OH}$ . One of them forms the chief ingredient in "fusel oil." This is formed during the fermentation of sugar solutions with yeast (wine, beer, etc.), and is present in freshly distilled spirits.

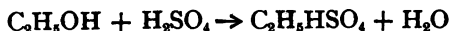


Waxes are compounds of a similar nature. They are formed, however, from the alcohols containing many carbon atoms (higher alcohols), and acids of a similarly complex nature. Thus spermaceti is cetyl palmitate,  $C_{15}H_{31}COOC_{16}H_{33}$ . Bees' wax is a mixture of cerotic acid,  $C_{27}H_{55}COOH$ , with myricyl palmitate,  $C_{15}H_{31}COOC_{26}H_{51}$ .

The so-called paraffin wax (p. 140) does not belong to this class. Some of the higher fats, such as Japan wax, are commercially known as waxes because they resemble them in appearance.

Fats are closely related to the ethereal salts, but they are of such importance that they will receive special treatment later.

**Olefines.**—When alcohol is mixed with concentrated sulphuric acid, heat is developed, owing to the combination of the alcohol with the acid, and the consequent formation of water. The compound produced by this reaction, however, is not ethyl sulphate,  $(C_2H_5)_2SO_4$ , but ethyl hydrogen sulphate,  $C_2H_5HSO_4$ , a compound corresponding to ammonium hydrogen sulphate or sodium hydrogen sulphate—



When this compound is heated it is decomposed as shown in the following equation—



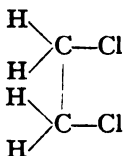
The hydrocarbon  $C_2H_4$  is called ethylene. In preparing it, there is no need to separate the ethyl hydrogen sulphate. It is sufficient to mix alcohol with concentrated sulphuric acid and heat the mixture. The gas is given off accompanied by small quantities of ether, and, as a certain amount of carbonisation always takes place, sulphur dioxide and carbon dioxide are also formed. These are removed by passing the gas through dilute alkali.

Ethylene is a hydrocarbon of a type different from the paraffins, for unlike these it can form compounds without parting with any hydrogen. For example, it combines directly with chlorine, forming no hydrochloric acid, but yielding an oily liquid of the formula  $C_2H_4Cl_2$ . In other words, chlorine

can be directly added to it. As this is possible it is obvious that the carbon in the compound is not combined with all that it could combine with. Ethylene is therefore an unsaturated hydrocarbon, its condition of unsaturation being shown by the fact that it takes up chlorine, without formation of hydrochloric acid, and forms an addition compound. *Saturated hydrocarbons can only form substitution compounds.*

The chlorine derivative is known as ethylene dichloride; we have previously met with a compound of the same empirical formula, but the two are very different in their properties. Dichlorethane  $C_2H_4Cl_2$  is represented by the formula  $CH_3CHCl_2$  (p. 145), but all experiments tend to prove that in ethylene dichloride the two chlorine atoms are combined with different carbon atoms, and its formula must therefore be written  $CH_2Cl.CH_2Cl$ .

This can be expressed graphically—



As ethylene is simply this compound without the chlorine, it might be written—



but this would suggest that carbon was trivalent, and would not show why it should take up chlorine so easily. We therefore write the formula—



<sup>1</sup> The lines drawn in these formulæ about the carbon atom and others must not be materialised in any way. The double bond in this formula does not signify that the two carbon atoms are tied together by two strings instead of one, or anything like that. It means rather, that in the compounds in which it appears, the carbon has a reserve valency which can be utilised when occasion arises. It is the *sign of unsaturation*.

By replacing a hydrogen atom in ethylene by methyl ( $\text{CH}_3$ ) we obtain another hydrocarbon,  $\text{C}_3\text{H}_6$ . This is known as propylene. Also by replacement of a hydrogen atom in propylene by  $\text{CH}_3$  we obtain  $\text{C}_4\text{H}_{10}$ , butylene, and so on. In short, we have another homologous series of hydrocarbons which may be represented by the general formula  $\text{C}_n\text{H}_{2n}$ .

The formation of the oily compound  $\text{C}_2\text{H}_4\text{Cl}_2$  when chlorine is added to ethylene, caused that gas to receive the name of olefiant<sup>1</sup> gas. The name with a modification is extended to the whole series. The hydrocarbons belonging to it are known as the Olefines.

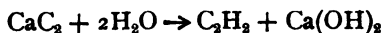
Ethylene is colourless, and insoluble in water. It burns with a brightly luminous flame, and its density compared with hydrogen is 14, *i.e.* its molecular weight is 28. (Note that it is only very slightly lighter than air.)

A still more unsaturated hydrocarbon is obtained by the direct union of carbon and hydrogen at the temperature of the electric spark. This compound is acetylene. It is a colourless gas with a disagreeable odour, poisonous, and burns with a brightly luminous flame. If burned without sufficient air supply it yields large quantities of soot.<sup>2</sup> Its density compared with hydrogen is 13, and its molecular weight therefore 26. This and its analysis show that its formula must be written  $\text{C}_2\text{H}_2$ . The gas can take up four atoms of chlorine forming a tetrachloride,  $\text{C}_2\text{H}_2\text{Cl}_4$ . Its condition of unsaturation is represented by its formula—



Acetylene is often formed when a bunsen burner "strikes back;" the odour can then be recognised.

As, however, the gas is largely used for illuminating purposes, a more convenient method of preparing a large quantity is used. This is the action of water upon calcium carbide,  $\text{CaC}_2$ —



<sup>1</sup> Lat. *oleum*, oil; *fio*, I become.

<sup>2</sup> See note A at the end of this chapter (p. 185).

As acetylene is represented by the formula—



calcium carbide must be  $\text{Ca} \begin{array}{c} \diagup \text{C} \\ ||| \\ \diagdown \text{C} \end{array}$

**Flame.**—The increasing luminosity of the flames of hydrogen, marsh gas, ethylene, and acetylene as the amount of carbon in the molecule is increased is significant. The flame of burning hydrogen is almost non-luminous, while that of acetylene burning under favourable conditions is of dazzling brightness.

The luminosity of flame is generally due to the presence of incandescent solid particles. A bunsen flame is almost non-luminous, but if a piece of platinum wire be suspended in it, the wire becomes white hot and emits light. The introduction of a solid into the flame for the purpose of producing luminosity is also seen in the case of the incandescent gas mantle. The flame in which the mantle hangs would be almost non-luminous, but the solid mantle glows brightly.<sup>1</sup>

If a piece of cold porcelain or glass be placed for a moment in an ordinary luminous gas flame, it becomes covered with a coating of soot, *i.e.* particles of carbon. This, however, scarcely shows the presence of solid particles in the flame, as the introduction of the cold substance may merely alter the condition existing in that part of the flame—it may cool the flame so that combustion partially ceases. The presence of solid particles in the luminous portion of a gas flame can, however, be inferred from the following experiment, which is best performed on a bright sunshiny day. As is well known, it is possible by means of a lens to form an image, say, of the sun upon a solid surface, but such an image cannot be formed

<sup>1</sup> These mantles are composed of a mixture of thorium oxide ( $\text{ThO}_2$ ) and cerium oxide ( $\text{CeO}_2$ ), 99 per cent. of the former and 1 per cent. of the latter.

The use of a solid to produce luminosity is also well seen in the lime-light, in which the hot flame of hydrogen or coal gas burning in oxygen is projected on to a cylinder of quick-lime.

upon a liquid or a gas. If now an ordinary bat's-wing burner be lighted, and a lens held near it in the sunshine, it will be found possible to focus an image of the sun as a highly luminous spot upon the brightest portion of the flame. This would not be possible unless the flame were solid, or contained huge numbers of solid particles acting as a solid screen. The experiment therefore proves that the luminous portion of such a flame contains solid particles, and as the ordinary burner burns coal gas, the only possible solid particles are those of carbon.<sup>1</sup>

It must not be assumed, however, that a flame cannot be luminous without solid particles. The flame of hydrogen becomes somewhat luminous when the gas and the oxygen in which it is burning are under pressure. Also, when carbon bisulphide burns in nitric oxide the flame is intensely luminous, and in this case no solids are present, and no extra pressure is applied to the gas.

In the case of the flames of methane, ethylene, and acetylene, the luminosity is due to the presence of unburnt particles of carbon, and as there is a larger percentage of carbon in acetylene than in the others, the flame of this gas is the most luminous of the three.

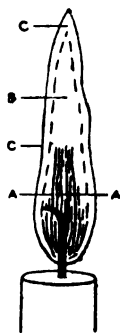


FIG. 18.

**Structure of the Flame.**—The flame of an ordinary candle may be taken as typical. It consists of three parts, which we will refer to as A, B, C.

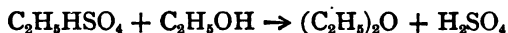
A is in appearance dark blue in tint. It consists of the volatilised hydrocarbons of which the candle is composed. It is not in contact with the oxygen of the air, and is therefore not within the area of combustion. B is the luminous portion. It surrounds A on all sides, and occupies the greater portion of the flame. It is the area of partial combustion, and it is here that the solid particles formed by decomposition of the material of the candle are to

<sup>1</sup> The brilliancy of the flame of burning magnesium is due to incandescence of the oxide formed.

be found. As they pass outwards they gradually reach the part of the flame where it is in direct contact with the oxygen of the air, and combustion becomes complete. This is the area C, which consists entirely of the incandescent products of combustion; in this case carbon dioxide and water vapour. These being gases are only faintly luminous and can barely be seen.

**The Bunsen Flame.**—Air is introduced into the middle of this flame, thereby causing complete combustion, not only at the outside but inside also. The solid particles are therefore absent, and the flame is much hotter.

**Ethers.**—When ethyl hydrogen sulphate is heated by itself it splits up into ethylene and sulphuric acid, but when heated with excess of alcohol a different change occurs; the products are sulphuric acid and ether—



Here again it is not necessary to prepare the ethyl hydrogen sulphate as a separate compound. It is sufficient to mix together sulphuric acid and alcohol, and heat the mixture. The temperature, however, must not exceed  $140^\circ\text{C}$ ., and alcohol should be continually added at such a rate as to keep the temperature constant at this point. If this is done, the evolution of ether is continuous, and it can be collected in a receiver as long as alcohol is supplied to the mixture.

The nature of this ether is most easily understood by comparing its constitutional formula with that of water and alcohol.

Water . . . . .	$\text{H}-\text{O}-\text{H}$
Alcohol . . . . .	$\text{C}_2\text{H}_5-\text{O}-\text{H}$
Ether . . . . .	$\text{C}_2\text{H}_5-\text{O}_2-\text{C}_2\text{H}_5$

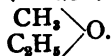
It will be seen that in the ether the hydroxyl hydrogen atom is replaced by another ethyl group. The ether bears much the same constitutional relation to the alcohol as potassium oxide bears to potassium hydroxide.

Again compare the formulæ—

Water . . . . .	$\text{H}-\text{O}-\text{H}$
Potassium hydroxide . . . . .	$\text{K}-\text{O}-\text{H}$
Potassium oxide . . . . .	$\text{K}-\text{O}-\text{K}$

Ordinary ether may therefore be looked upon as the oxide of ethyl, and other ethers as the oxides of other organic radicles. Ethers, however, have no basic properties which are in any degree comparable with those of basic oxides.

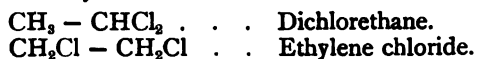
Many other ethers are known; such are methyl ether  $(\text{CH}_3)_2\text{O}$ , propyl ether  $(\text{C}_3\text{H}_7)_2\text{O}$ , and methyl ethyl ether



The ether commonly found in the laboratory is ethyl ether. As, however, it is prepared from methylated spirit it is not quite pure, but contains a minute quantity of methyl ether. It is a limpid, neutral, mobile liquid. It is highly volatile, its boiling point being  $34.9^\circ \text{C}$ . It burns with a luminous flame, and the mixture of its vapour with air is highly explosive. It is somewhat soluble in water, and water is slightly soluble in ether. Its chief uses in the laboratory arise from the facility with which it dissolves fats and oils, and many other organic compounds. It does not act as a solvent towards inorganic compounds.<sup>1</sup> It is therefore used for the extraction of fats, from which it is easily separated by distillation.

Ether, as generally supplied, contains a considerable quantity of water and some alcohol; but both of these impurities are removed by prolonged contact with calcium chloride. The last traces of water can be taken away only by the addition of metallic sodium.

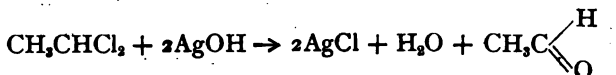
**Polyhydric Alcohols.**—It has been shown that dichlorethane and ethylene chloride are both represented by the same empirical formula,  $\text{C}_2\text{H}_4\text{Cl}_2$ . The difference in properties has been traced to a difference in constitution. In the former the two atoms of chlorine are attached to the same carbon atom, in the latter they are attached to the different ones. This is indicated by the constitutional formulæ—



When monochlorethane,  $\text{C}_2\text{H}_5\text{Cl}$  (ethyl chloride), is treated with silver hydroxide, the chlorine is replaced by hydroxyl and ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) is formed. It might be expected

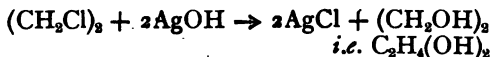
<sup>1</sup> See note B at the end of this chapter.

therefore, that when dichlorethane is treated in a similar way each of the chlorine atoms would be replaced by hydroxyl. As a matter of fact this does *not* occur; water is always formed, and the product obtained is aldehyde—



It may be taken as a rule, to which there are very few exceptions, that more than one hydroxyl group is never attached to the same carbon atom.<sup>1</sup>

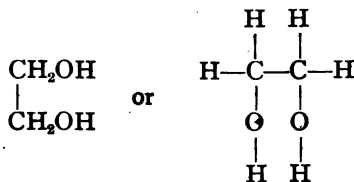
When ethylene dichloride is treated with silver hydroxide (moist silver oxide) each of the atoms of chlorine is replaced by hydroxyl. The product is called glycol—



As ethylene dichloride may be represented thus—



glycol may likewise be expressed thus—



Any compound which contains hydroxyl attached to a carbon atom not otherwise oxidised has the characteristic properties of and is classed as an alcohol. It will be seen, therefore, that glycol is a double alcohol, or as it is commonly called, a dihydric alcohol. Just as the alcohols previously described were compared to the hydroxide of the monovalent

<sup>1</sup> The non-existence of stable carbonic acid is an instance. Its formula  $\text{H}_2\text{CO}_2$  would be  $\begin{array}{c} \text{HO} \\ \diagdown \\ \text{C} = \text{O} \\ \diagup \\ \text{HO} \end{array}$ .

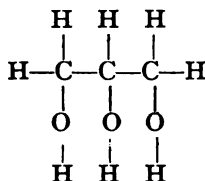


metal potassium KOH, so glycol and other dihydric alcohols may be compared to the hydroxide of a divalent metal such as calcium,  $\text{Ca}(\text{OH})_2$ .

It was pointed out that the term "alcohol" was extended to include the whole class of the monohydroxyl derivatives similar to "spirit of wine." In like manner the term "glycol" is extended to include all the dihydric alcohols; they are known as glycols.

Trihydric alcohols containing three hydroxyl groups are known. As no two hydroxyl groups can be attached to the same carbon atom, the simplest trihydric alcohol must contain three carbon atoms. It will be  $\text{C}_3\text{H}_7(\text{OH})_3$ .

This is glycerine. Its structural formula may be written—



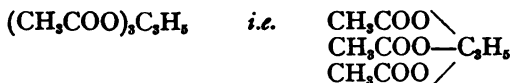
or



For the sake of uniformity in nomenclature, and to retain names ending in "ol" for hydroxyl derivatives, glycerine is generally referred to in chemistry as glycerol.<sup>1</sup>

Glycerine or glycerol is a colourless syrupy liquid, with a very sweet taste. It dissolves in alcohol and in water in any proportion, and takes up moisture from the air.<sup>2</sup> It cannot be distilled at ordinary pressure as it undergoes decomposition.

Glycerol may be compared to the hydroxide of a triad metal, such as aluminium,  $\text{Al}(\text{OH})_3$ . It will form salts, with acids as the mono and dihydric alcohols do; the triacetate may be taken as an example. Its formula is—



<sup>1</sup> Gk. *γλυκός*, sweet.

<sup>2</sup> As glycerine does not dry or resinise, it is used in making ink for use with rubber stamps, also for certain forms of copying inks.

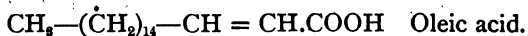
**Fats, Oils, and Soap.**—Most people know that soap is made by boiling fats with soda. Many of the older generation of country folk were accustomed to make their own soap in this way. Glycerol is produced at the same time. Ordinary soap consists largely of sodium stearate, *i.e.* the sodium salt of stearic acid. Stearic acid is one of the higher members of the homologous series to which acetic acid belongs, and to which the general formula  $C_nH_{2n+1}COOH$  has been assigned. Its formula is  $C_{17}H_{35}COOH$ .

large proportion of palmitin and stearin are solid. Mutton fat, beef fat, and lard are rich in stearin. Palmitin is so called because it occurs in palm oil, whence also the name palmitic acid. In this country palm oil is generally solid.

Glycerides of other acids often occur in oils. Thus, drying oils, such as linseed oil, hemp oil, poppy oil, contain the glyceride of linoleic acid,  $C_{18}H_{32}O_2$ . These oils resinise on exposure to the air, by oxidation. Castor oil contains the glyceride of ricinoleic acid,  $C_{18}H_{34}O_3$ .

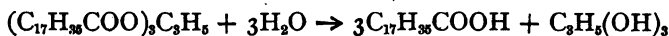
As vegetable or animal oils are glycerides and are saponified on boiling with soda, they can easily be distinguished from mineral oils, such as paraffin, vaseline, etc., which are hydrocarbons, and yield no soap when boiled with soda, in fact, soda is without action upon them.

It will be noticed that the formula of stearic acid,  $C_{18}H_{36}O_2$ , and that of palmitic acid,  $C_{16}H_{32}O_2$ , both correspond to the general formula of the homologous series,  $C_nH_{2n}O_2$  (p. 152), but the formula of oleic acid,  $C_{18}H_{34}O_2$ , does not. This acid is not a member of the series. It contains the same number of carbon atoms as stearic acid, but lacks two atoms of hydrogen. Oleic acid, in fact, is an unsaturated compound. It bears the same relation to stearic acid as ethylene bears to ethane. This can be represented in their constitutional formulæ—



Like ethylene, oleic acid can form addition compounds with chlorine, iodine, etc.

In the manufacture of soap on a commercial scale, the fat is decomposed with superheated steam—

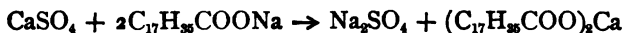


By this process the fatty acid itself is liberated. It is then neutralised with soda or potash, and the soap produced is precipitated with concentrated salt solution, in which it is insoluble. The aqueous solution is then drawn off, and the glycerol, which commands a high price, is recovered from it. A certain amount of resin is generally introduced into ordinary soaps to make them firmer and dryer.

Transparent soaps are made by dissolving the soap in alcohol and evaporating the solution.

Potash soaps are called soft soaps. They are softer and more soluble in water than soda soaps. When soaps are dissolved in water they undergo partial hydrolysis, so that they all show an alkaline reaction to litmus. Lime, lead, and other bases may be substituted for soda or potash, but the soaps so produced are insoluble in water. Lead soap is known generally as lead plaster. Ammonia soaps are used for some laundry purposes.

The fact that soaps are salts of certain fatty acids provides an explanation of the effect of "hard" water upon them. As previously stated (p. 69), such water usually contains salts of calcium and magnesium, and these, with the soap, undergo a double decomposition; for instance—



The calcium salt (stearate in this case) forms a solid scum upon the water. All the lime must be precipitated in this way before a lather can be produced.<sup>1</sup>

Magnesium salts act in a precisely similar manner, but their immediate effect on the soap is not so marked, a "false lather" being produced before all the magnesium is precipitated. It is, however, temporary.

The "hardness" of water caused by the presence of mineral acids (an unusual form of hardness), is due to the decomposition of the soap and consequent liberation of the free acid—



**Isomerism.**—In studying the compounds of carbon, we meet with many which are composed of the same elements combined in the same proportions by weight. Such compounds are said to be Isomeric.<sup>2</sup>

Now, if two or more compounds consist of the same elements in the same proportion by weight and yet differ in their properties, the elements must be combined in a different

<sup>1</sup> See note C at the end of this chapter.

<sup>2</sup> Gk. *isos*, equal; *meros*, a share.

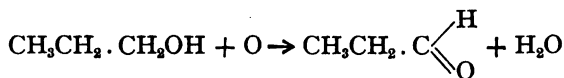
manner. That such a difference exists in many organic compounds has been confirmed by a multitude of experiments.

If, in methane ( $\text{CH}_4$ ), we replace one of the hydrogen atoms by hydroxyl we obtain methyl alcohol. Experiment has shown that it does not matter which of the hydrogen atoms is substituted; the same compound is produced in all cases.

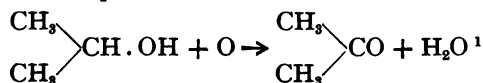
Similarly with ethane ( $\text{CH}_3\text{—CH}_3$ ), any one of the six hydrogen atoms may be replaced by hydroxyl, but only one ethyl alcohol is produced.

The hydrocarbon propane is  $\text{C}_3\text{H}_8$ , *i.e.*  $\text{CH}_3\text{—CH}_2\text{—CH}_3$ . By replacing one of the eight hydrogen atoms by hydroxyl we obtain, of course, propyl alcohol, but now we find that instead of obtaining one such compound only, we obtain two, differing in their physical and chemical properties. They boil at different temperatures, and on oxidation produce different compounds. Careful examination of these alcohols has shown that one of them must be represented by the formula  $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{OH}$ , and the other by the formula  $\text{CH}_3\text{.CHOH—CH}_3$ . The first of these is *normal* propyl alcohol. In this the hydroxyl replaces a hydrogen in either one of the methyl groups ( $\text{CH}_3$ ). The second is known as *iso*-propyl alcohol: here the hydroxyl replaces a hydrogen of the group  $\text{CH}_2$ .

If normal propyl alcohol be oxidised it yields first propyl aldehyde and then propionic acid—



If, however, isopropyl alcohol be oxidised no aldehyde is formed, but a compound of a somewhat different nature—



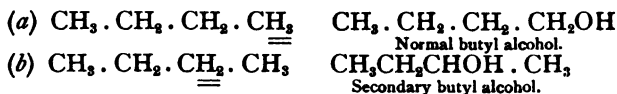
This compound is called acetone. It is the oxygen compound corresponding to the dichlor derivative  $\text{CH}_3\text{.CCl}_2\text{.CH}_3$ . It is present in crude wood-spirit. Other similar compounds are known, and the name *Ketone* is given to the class.

<sup>1</sup> Further oxidation does not lead to the formation of a corresponding acid.

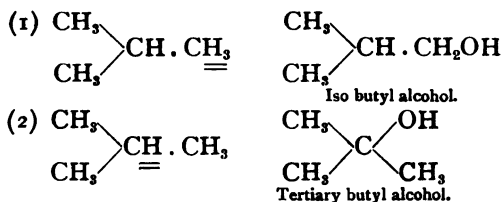
The two alcohols, normal propyl alcohol and isopropyl alcohols, are isomeric.

Isomerism is, of course, not confined to alcohols. Any class of compounds may exhibit it, and, in fact, isomeric bodies may belong to totally different classes of compounds. All the paraffin hydrocarbons above propane, give multitudinous examples of isomerism. Butane, for example, is  $C_4H_{10}$ , and two compounds of this formula are known. They are called normal butane and isobutane; the first  $CH_3-CH_2-CH_2-CH_3$ , and the second  $\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CH \cdot CH_3$ . If now we replace one of the hydrogens in these compounds by hydroxyl four separate butyl alcohols can be produced.

(1) From normal butane.



(2) From isobutane—



All these alcohols are isomeric. They represent three classes of alcohols.

(a) Those in which hydroxyl takes the place of a hydrogen atom in the group  $CH_3$ , and which consequently contain the group  $CH_2OH$  are called *primary* alcohols.

(b) Those in which the hydroxyl takes the place of a hydrogen atom in the group  $CH_2$ , and which consequently contain the group  $CHOH$ , are called *secondary* alcohols.

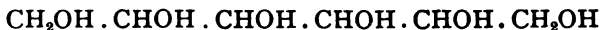
- (c) Those in which the hydroxyl takes the place of a hydrogen atom in the group CH, and which therefore contain the group COH are called tertiary alcohols.

Tertiary alcohols do not yield either aldehyde or corresponding acid on oxidation. A special kind of isomerism is known as *polymerism*. This is found in the case of compounds consisting of the same elements in the proportion by weight, but which differ in their molecular weight. Thus, acetylene  $C_2H_2$  and benzene  $C_6H_6$  are polymeric, so are aldehyde, paraldehyde (p. 150), and aldol (p. 151).

It will be seen that isomerism greatly increases the possible number of carbon compounds of all classes.

**Carbohydrates.**—Secondary and tertiary alcohols must not be confused with dihydric and trihydric alcohols. The latter are those which contain two and three hydroxyl (OH) groups respectively. Alcohols containing 4, 5, and 6 hydroxyl groups are also known. The last are called hexahydric alcohols. They are of special interest from the present point of view. It was shown (p. 163) that the several hydroxyl groups, when there is more than one, are always attached to different carbon atoms.

Hexahydric alcohols can, therefore, be derived only from hydrocarbons which contain at least six atoms of carbon. The formula for such a hexahydric alcohol may therefore be written—



Such a compound is evidently both a primary and secondary alcohol, for it contains both the groups  $CH_2OH$  and  $CHOH$ —it belongs to both classes.

If either of the carbon atoms at the ends of the chain be oxidised the product, while still remaining an alcohol, will also be an aldehyde. If any other of the carbon atoms be oxidised the product, while still remaining an alcohol, will also be a ketone (p. 168). Compounds of both types are well known. They occur plentifully in fruits and vegetables of various kinds, and are called sugars. The aldehyde type of sugar is

represented by glucose (grape sugar), the ketone type by fructose (fruit sugar). Their formulæ can be written—



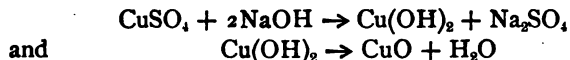
and



It will be seen that both substances can be represented by the empirical formula  $\text{C}_6\text{H}_{12}\text{O}_6$ . They are therefore isomeric.

Glucose and fructose are very similar in many respects. They are crystalline bodies, soluble in water, of neutral reaction, have a sweet taste, and are easily caramelised (*i.e.* charred) by heat.<sup>1</sup> Both substances are readily oxidised and therefore act as reducing agents towards various metallic salts.

This is plainly seen in their action upon cupric hydroxide. If, to a solution of cupric salt, some caustic soda be added, cupric hydroxide is thrown down as a greenish-blue precipitate, which on boiling becomes black owing to its conversion into cupric oxide.



If, however, glucose be added to the copper sulphate solution and then caustic soda, boiling throws down a red or yellow precipitate of cuprous hydroxide  $\text{Cu}_2\text{O}$ , the cupric hydroxide being reduced by the glucose which is itself oxidised. The oxidation of glucose by this method is somewhat complicated and leads to the formation of several compounds.

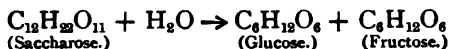
For convenience this reduction of cupric salts by glucose and fructose is done with Fehling's solution, which is a mixture of cupric sulphate, Rochelle salt,<sup>2</sup> and potassium or sodium hydroxide.

<sup>1</sup> They are both optically active, *i.e.* they rotate the direction of the vibration of a beam of polarised light.

<sup>2</sup> Rochelle salt is potassium, sodium, tartrate.  $\left. \begin{array}{l} \text{CHOHCOOK} \\ \text{CHOHCOONa} \end{array} \right\}$ . It is added, because tartrates prevent the precipitation of copper by alkalis.



Ordinary household sugar (saccharose) was formerly obtained exclusively from sugar cane. It is still commonly called cane sugar, though large quantities are now produced from sugar beet. The sugar, however, obtained from sugar beet is identical, when purified, with that obtained from sugar cane. Its composition is represented by the formula  $C_{12}H_{22}O_{11}$ . It does not as such reduce Fehling's solution, but when boiled with dilute acids it breaks up into glucose and fructose—



It will be seen that the cane sugar is hydrolysed in the presence of acids. The change of saccharose into glucose and fructose is thus easily carried out, but no means has yet been discovered by which the process can be reversed. Despite this fact, saccharose is generally regarded as a compound of glucose with fructose minus a molecule of water.

Another sugar of the empirical formula  $C_{12}H_{22}O_{11}$  occurs in milk; it is known as lactose. It is not so soluble in water as cane sugar, neither is it so sweet. It is more readily decomposed by heat, and *reduces Fehling's solution*. When boiled with dilute acids it undergoes hydrolysis, but the products are glucose and galactose. Galactose<sup>1</sup> is a sugar of the same empirical formula as glucose  $C_6H_{12}O_6$ , with which it is therefore isomeric.

One more sugar of the formula  $C_{12}H_{22}O_{11}$  is of importance, it is *maltose*. This is formed by the action of malt on starch. When hydrolysed it yields two molecules of glucose.

All sugars undergo fermentation by the action of yeast and other organisms (p. 174), but it is probable that sugars of the formula  $C_{12}H_{22}O_{11}$  undergo hydrolytic change before the formation of alcohol from them can take place.

The sugars are merely a sub-division of a larger class of compounds called carbohydrates. This name owes its origin to the fact that all the compounds originally included in the group consist of carbon, hydrogen, and oxygen only, and the hydrogen and oxygen are always present in the proportion in which they are present in water.

<sup>1</sup> Gk. γάλα, milk.

Next to the sugars, the most important members of the carbohydrate group are starch, cellulose, and dextrine. The composition of all these compounds is represented by the empirical formula  $C_6H_{10}O_5$ . When starch is boiled with dilute acid, it is converted into glucose as shown in the equation—



A similar result is produced by the action of diastase—a ferment which occurs in malt, and in smaller quantities in most other starchy seeds and vegetables. In this case the starch appears to be first converted into dextrine, and, by properly regulating the conditions, a large amount of dextrine can be produced in this way.

Dextrine is an amorphous substance soluble in water, and of neutral reaction. By the further action of diastase, or by boiling with dilute acids, it is converted into glucose. Dextrine may also be prepared from starch by heating it in the dry condition. It is used as the gum on the backs of postage stamps.

Several forms of cellulose are known, the most familiar is, perhaps, cotton-wool. Good quality filter-paper is almost pure cellulose. Cellulose is not changed by dilute acids to any appreciable extent, but strong sulphuric acid converts it into glucose.

Starch occurs largely in nearly all plants and their seeds in the form of minute grains. It is chiefly prepared from various forms of grain and from potatoes. Starch grains vary considerably in shape, so that it is generally possible to tell from the form of the starch-grain from what plant the starch was obtained.

Starch is insoluble in cold water. If, however, it is heated with water, the outer membranes of the starch cells (grains) are broken, and the contents form a mucilage or partial solution.

The usual test for starch is provided by the action of iodine upon it. This forms with starch a deep blue coloured compound. The colour disappears on warming, but returns on cooling.

Since glucose is formed from starch, cellulose<sup>1</sup> and dextrine by the addition of water—that is, the effect of the acid—it might be expected that they could be obtained by abstraction of a molecule of water from glucose, but no means is known by which this reverse change can be accomplished.

**Fermentation.**—The fermentation of glucose by yeast or other organisms (p. 172), resulting in the formation of alcohol, takes place in a manner which can be represented, in so far as it concerns the chief products, by the equation—



Under the microscope yeast can be seen as a unicellular organism. During its growth it often forms branching chains of cells. The fermentation of the sugar accompanies the growth of the yeast, and, therefore, the sugary liquid must also contain some nitrogenous material to supply nitrogen for the cell contents of the organism. Without this nitrogenous material the yeast could not grow, and fermentation would not take place. For this reason pure sugar solution does not undergo fermentation. Alcohol is, therefore, to some extent, a product of the life of the yeast. It will not proceed indefinitely, for when alcohol has attained a certain concentration it arrests the action of the organism.

Temperature has also a great effect upon the rapidity of alcoholic fermentation. The most suitable is about 60° C.

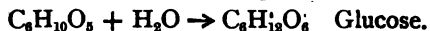
Many other kinds of fermentation are known; such as the acetic acid fermentation (p. 153), the lactic and the butyric acid fermentations (p. 178). They are all brought about by certain unstable chemical compounds known as enzymes. It was formerly the custom to distinguish two classes of ferments—organised and unorganised; the former including yeast and

<sup>1</sup> Cellulose (cotton wool) when treated with a mixture of nitric and sulphuric acids for twenty-four hours forms gun-cotton. The appearance of the cotton is not appreciably changed, but the substance has become extremely explosive. It is now cellulose hexanitrate,  $C_{12}H_{14}O_4(NO_3)_6$ . Mixed with camphor it forms the chief constituent of celluloid. Celluloid is highly inflammable.

<sup>2</sup> In the case of effervescent or “sparkling” wines, etc., much of the fermentation is allowed to go on after bottling, so that the liquid becomes charged with carbon dioxide under pressure.

other living organisms, and the latter such materials as diastase (p. 173). It has, however, been shown that this distinction is scarcely sound, as the function of the "organised ferment" is to produce the enzyme which causes the fermentation to take place. Alcoholic fermentation, for example, has been brought about by means of the expressed juices from yeast, in the absence of living cells. The juices contain the enzyme, and fermentation accordingly takes place. It will not of course proceed far, as the absence of living yeast prevents the formation of fresh enzyme. In the case of yeast the enzyme is known as zymase.<sup>1</sup>

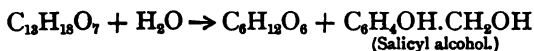
The action of enzymes upon starch is an important form of fermentation. The change is similar to that produced when the substance is boiled with dilute acids. The action of diastase on starch is a simple example—



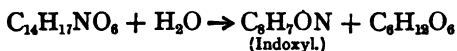
Other and perhaps more typical instances are to be found in the decomposition of the glucosides (derivatives of glucose), which occur so largely in plants. To bring about the hydrolytic change, a special ferment (enzyme) seems to be required in each case, but this always occurs in the plant associated with the glucoside.

The following are a few examples of glucosides and the manner in which they decompose under the action of special ferments.

(a) Salicin,  $C_{13}H_{18}O_7$ , occurs in willow-bark. Under the action of an enzyme it hydrolyses as follows:—



(b) Indican,  $C_{14}H_{17}NO_6$ , occurs in woad—



Indoxyl is readily oxidised to indigo blue,  $(C_8H_5ON)_2$ .

(c) Amygdaline,  $C_{20}H_{27}NO_{11}$ , occurs in bitter almonds (p. 190), also in the kernels of peaches, cherries, etc., and in the pips of apples and pears—

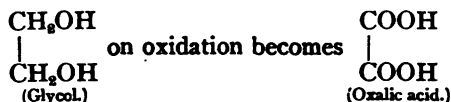


<sup>1</sup> See note D at the end of this chapter.

(d) Saponin,  $C_{22}H_{34}O_{10}$ , is extracted from Soap Root (*saponaria officinalis*); it forms a lather with water like that produced by soap. Mixed with vegetable refuse it is used as a worm-killer on lawns, etc. It is said to be occasionally added to ginger beer to produce a frothy appearance.<sup>1</sup>

(e) Some of the substances known as "tannins" are also glucosides, and the bi-hexose sugars ( $C_{12}H_{22}O_{11}$ ) may also be regarded as belonging to that class.

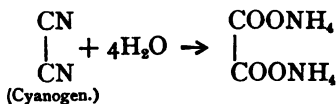
**Dibasic Acids.**—It was shown (p. 163) that glycol,  $C_2H_4(OH)_2$ , is a double or dihydric alcohol. Either or both of the carbon atoms can be oxidised. In the latter case we obtain a double, *i.e.* a dibasic, acid called oxalic acid—



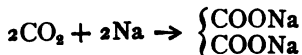
This acid is best prepared by the action of concentrated nitric acid upon sugar, and other organic materials such as starch and cellulose. It is manufactured on a large scale by heating sawdust with caustic soda to a temperature of about  $250^\circ \text{C}$ . In this case the sodium salt is of course formed.

Two other methods of formation are of some importance.

(1) If a solution of cyanogen gas (p. 179) in water is kept for some time, it spontaneously undergoes decomposition and forms ammonium oxalate.



(2) If dry carbon dioxide be passed over metallic sodium, sodium oxalate is produced—



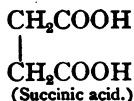
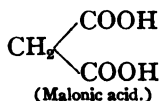
The acid is generally sold in crystals containing two molecules of water of crystallisation,  $C_2H_2O_4 \cdot 2H_2O$ . It is widely distributed in plants, occurring in several of the *oxalis* varieties (wood sorrel, *Oxalis acetocella*), as the acid potassium

<sup>1</sup> See note E at the end of this chapter.

salt.<sup>1</sup> Calcium oxalate is also found in clovers and many other plants.

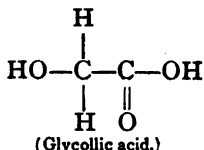
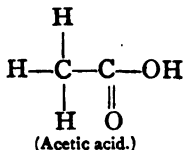
Oxalic acid and its soluble salts are poisonous.

All substances which contain the group ( $\text{—COOH}$ ) carboxyl have acidic properties. Those which contain two such groups are dibasic. Similar acids are derived from propane, butane, and other hydrocarbons. In fact, there is a homologous series of dibasic acids. Malonic and succinic acid may be taken as examples. The latter can be obtained from amber.



**Hydroxy Acids.**—If only one of the carbon atoms in glycol be oxidised, only one carboxyl group is formed, and the product is therefore a monobasic acid. It is called glycollic acid. Now, since glycol is a dihydric alcohol, and only one of the hydroxyl groups is changed into carboxyl, the other continues to exist in the compound, and cause it to exhibit the properties of an alcohol. In short, glycollic acid is at once an acid and an alcohol.

On reference to the structural formulæ it will be seen that glycollic acid is acetic acid in which an atom of hydrogen is replaced by hydroxyl. For this reason it is often called hydroxy-acetic acid.



Glycollic acid is found in nature in unripe grapes, etc.

Many other hydroxy acids—both monobasic and dibasic—are known. Many of them occur in nature, especially in

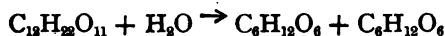
<sup>1</sup> This salt  $\left\{ \begin{array}{l} \text{COOH} \\ \text{COOK} \end{array} \right.$  is prepared artificially and sold as "Salts of sorrel." It is used for removing inkstains, etc.

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fruits and in plants of various kinds. Among the most important is lactic acid, which is hydroxy propionic acid.



This substance is produced by the fermentation of milk sugar. The lactose seems to be first hydrolysed with the formation of glucose and galactose—



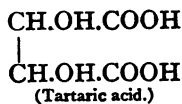
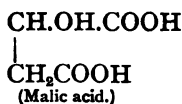
These sugars then undergo decomposition—



The fermentation does not, however, stop here, but proceeds to the formation of butyric acid<sup>1</sup>—



Two hydroxy succinic acids are known. They are—



Malic acid (mon-hydroxy-succinic acid) occurs in apples, strawberries, and many other fruits. Tartaric acid (di-hydroxy-succinic acid) occurs in grapes, in berries of the mountain ash, and in other plants. It can be made by oxidising lactose with nitric acid, but is generally prepared from "argol," which is impure potassium hydrogen tartrate. This salt crystallises out when grape juice ferments. It is purified by recrystallisation, and is then known as cream of tartar.<sup>2</sup> Cream of tartar is largely used in the manufacture of baking powder.

Only one tribasic acid need be mentioned. This is citric acid. It occurs largely in oranges, lemons, and similar fruits; it is  $\text{C}_3\text{H}_4\text{OH}(\text{COOH})_3$ .

<sup>1</sup> Butyric acid is a liquid which mixes with water in all proportions. It has an odour resembling that of rancid butter.

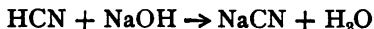
<sup>2</sup> Argol is sometimes known as tartar.

**Nitrogenous Compounds.**—When any nitrogenous carbon compound is heated with metallic sodium,<sup>1</sup> the metal combines with both the carbon and the nitrogen and forms a compound known as sodium cyanide (NaCN).

Commercially, cyanides are produced from organic refuse such as waste hair, hides, or dried blood, by fusing them with scrap iron and potassium carbonate. The fused mass is washed out with water, and from the solution a crystalline salt, potassium ferrocyanide,<sup>2</sup>  $K_4FeC_6N_6$ , may be easily obtained. This is the potassium salt of hydroferrocyanic acid,  $H_4FeC_6N_6$ . When this cyanide is heated with dilute sulphuric acid an extremely poisonous gas, known as hydrocyanic acid (HCN), is given off.

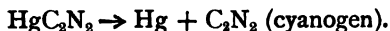
It will be remembered that when potassium ferrocyanide is heated with *concentrated* sulphuric acid, carbon monoxide is evolved.

Hydrocyanic acid is soluble in water, and the solution has an acid reaction. When neutralised with bases it forms cyanides—



Many of the cyanides are soluble in water. Others, such as silver cyanide, are insoluble.

If hydrocyanic acid be neutralised with precipitated mercuric oxide, mercuric cyanide is formed. This substance, which is a white crystalline solid, is decomposed on heating, yielding mercury and cyanogen gas—



This gas is colourless, and burns with a peculiar pink-coloured flame. It is somewhat soluble in water, and highly poisonous.

<sup>1</sup> Some compounds do not contain sufficient carbon to give this reaction. The difficulty can be surmounted by adding a little sugar to the mixture.

<sup>2</sup> The name is short for potassium ferrous cyanide, for the compound may be considered as a double cyanide,  $4KCN.FeC_2N_2$ , *i.e.* four mols. of potassium cyanide combined with one mol. of ferrous cyanide.

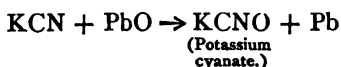
<sup>3</sup> Gk., *κύανος*, blue. The name cyanogen was given to the compound because many of its derivatives are blue in colour.



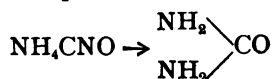
While cyanogen gas is  $C_2N_2$ , *i.e.*  $\begin{array}{c} C \equiv N \\ | \\ C \equiv N \end{array}$ , the term cyanogen is generally given to the unsaturated group  $-C \equiv N$ , which often enters into combination in organic compounds.

Hydrocyanic acid is also known as prussic acid. It contains the group  $-C \equiv N$ , and its formula can be written  $H-C \equiv N$ .

The cyanides are powerful reducing agents. When, for instance, potassium cyanide is fused with red lead or litharge, the lead oxide is reduced to metallic lead and the cyanide is oxidised to cyanate—



From potassium cyanate a most important salt can be obtained by double decomposition. This is ammonium cyanate. It is prepared by adding ammonium sulphate to a solution of potassium cyanate. From strong solutions the potassium sulphate would be largely precipitated, and the ammonium cyanate remain in solution. The ammonium salt, however, cannot be crystallised, for if the solution be allowed to stand it gradually undergoes transformation. The change is more rapidly brought about by heating. It is a rearrangement of the elements in the compound—



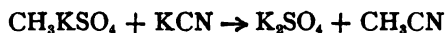
The compound produced is known as carbamide or urea. It is found in the urine of all mammals, particularly those whose food consists wholly or partially of flesh. In fact, it is the compound in the form of which the waste nitrogen of the body is chiefly excreted.<sup>1</sup>

The above preparation of urea is of importance, as it afforded the first instance of the formation in the laboratory of a carbon compound which was known to be present in the animal body, and which was supposed to be the product of

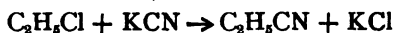
<sup>1</sup> Uric acid,  $C_5H_4N_4O_6$  (a somewhat complex compound), also occurs in urine.

vital force. Since its preparation in 1828, many other compounds which occur in plants and animals have been prepared by artificial means, and "organic chemistry" no longer means the chemistry of the compounds produced by organised bodies, but merely the chemistry of the carbon compounds.

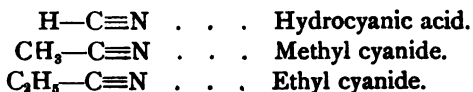
Cyanides of metals are not the only cyanides which are known. When, for instance, methyl potassium sulphate,  $\text{CH}_3\text{KSO}_4$  (p. 156), is heated with potassium cyanide a simple reaction takes place resulting in the formation of methyl cyanide—



A similar compound may be obtained from ethyl compounds such as ethyl chloride—

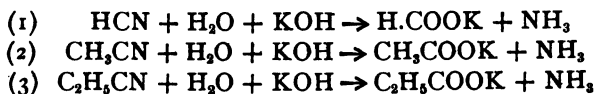


and in fact a homologous series of cyanides can be obtained, of which the first three members are—



The importance of these compounds lies in the ease with which they undergo hydrolysis in the presence of caustic alkali—

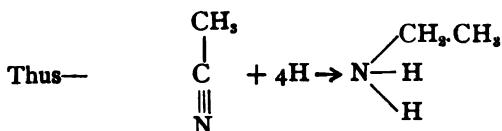
(1)  $\text{H.CN} + 2\text{H}_2\text{O} \rightarrow \text{H.COONH}_4$ , ammonium formate ;  
or, in the presence of alkali—



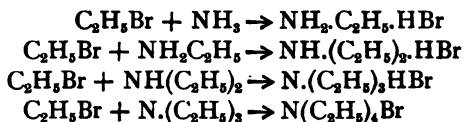
It will be seen therefore that hydrocyanic acid, when hydrolysed, gives salts of formic acid ; methyl cyanide gives acetates ; and ethyl cyanide, propionates. For this reason these cyanides are often called the nitriles of the acids produced by hydrolysis. Hydrocyanic acid is formo-nitrile ; methyl cyanide is aceto-nitrile, etc.

When these nitriles are treated with nascent hydrogen, *i.e.* when hydrogen is liberated in their solution (by adding zinc

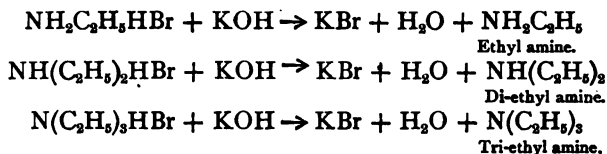
and hydrochloric acid), they are reduced to a class of bodies known as Amines.



The amines can also be prepared by treating the halogen derivative of a hydrocarbon with ammonia. When, for example, monochlorethane, or, preferably, the bromine compound  $\text{C}_2\text{H}_5\text{Br}$ , is used, successive replacements of the hydrogen in the ammonia take place, and four different compounds are produced—



The compounds produced by these reactions may be considered as ammonium bromide,  $\text{NH}_4\text{Br}$ , in which the atoms of hydrogen are successively replaced by  $\text{C}_2\text{H}_5$ . They are therefore known as ethyl ammonium bromides. When treated with caustic potash or soda they behave in many respects like ammonium salts—



From the compound  $\text{N}(\text{C}_2\text{H}_5)_4\text{Br}$ , a compound corresponding to ammonium hydroxide can be obtained; it is tetra ethyl ammonium hydroxide  $\text{N}(\text{C}_2\text{H}_5)_4\text{OH}$ .

The amines are generally regarded as ammonia in which one or more atoms of hydrogen have been replaced by an equivalent amount of  $\text{C}_2\text{H}_5$ . Their properties are very similar to those of ammonia. They are soluble in water, yielding alkaline solutions, and combine with acids to form salts.

Similar compounds can be prepared having the same relationship to other hydrocarbons as the ethyl amines have to ethane; *e.g.* methyl amines,<sup>1</sup> propyl amines, etc. There is, therefore, a homologous series of each of the amines, mono, di, and tri.

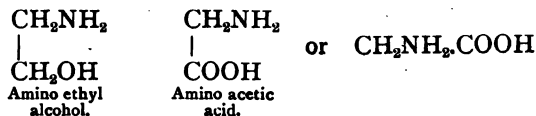
By treatment of glycol with hydrochloric acid, glycol monochloride (ethylene chlorhydrin)—



is formed, and this reacts with ammonia like ethyl bromide, *i.e.* the two substances combine, forming hydroxy-ethyl ammonium chloride, from which hydroxy-ethylamine may be obtained by the action of caustic potash.

Hydroxy-ethylamine may be regarded as ethyl alcohol in which an atom of hydrogen is replaced by  $\text{NH}_2$ , *i.e.* it is at once an amine and an alcohol. It is therefore often referred to as amino-ethyl alcohol.

Just as acetic acid is produced by the oxidation of ethyl alcohol, so when the amino alcohol is oxidised, amino-acetic acid is produced—



Amino-acetic acid is a crystalline substance, readily soluble in water; it has both acid and basic properties, uniting with acids to form salts, and with bases to form other salts, the amino-acetates. This may be attributed to the fact that the amino group  $\text{NH}_2$  is basic, and the carboxyl group  $\text{COOH}$  is acidic.

<sup>1</sup>  $\text{NH}_2\text{CH}_3$ . Gaseous compound, very soluble in water, strongly alkaline.

$\text{NH}(\text{CH}_3)_2$ , di-ethyl amine. Gas, easily condensed to a liquid.

$\text{N}(\text{CH}_3)_3$ , tri-ethyl amine. Liquid, b.p. about  $9^\circ \text{C}$ .

Occurs in herring-brine, also as the liquids obtained during the refining of beet sugar. The odour of methyl amine, similar to that of ammonia, can often be detected in very large quantities of beet sugar.

Amino acetic acid, being derived from glycol, is very often called glycocoll, glycocine, or glycine.<sup>1</sup> By replacing one of the hydrogen atoms of the  $\text{CH}_2$  group in the above formula by  $\text{CH}_3$ , amino propionic acid<sup>2</sup> can be obtained. The properties of the amino propionic acids are very similar to those of glycocoll.

The amines and amino acids above described must be distinguished from another class of compounds known as acid-amides.

When ammonium acetate,  $\text{CH}_3\text{COONH}_4$ , is heated in the dry state, water is given off and a substance known as acetamide,  $\text{CH}_3\text{CONH}_2$ , is produced—

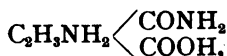


This substance may be regarded as ammonia in which an atom of hydrogen is replaced by the acid radicle,  $\text{CH}_3\text{CO}$ , or, better, as acetic acid in which the hydroxyl is replaced by  $\text{NH}_2$ .

It can also be obtained by treating an ethereal salt of acetic acid with ammonia—



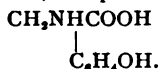
Acetamide is a crystalline substance soluble in water, and has neither acid nor basic properties. The amides of other acids may be prepared in a similar manner. The well-known compound asparagine is the amide of amino succinic acid—



It is found in asparagus, peas, beans, etc.

**Albuminoids and Proteins.**—White of egg, milk curd (casein),<sup>3</sup> red flesh or muscular tissue, skin, etc., are very

<sup>1</sup> A derivative of amino-acetic acid is largely used as a photographic developer, and is sold under the name of glycine. It is, however, not the compound mentioned in the text; it is para-oxyphenyl glycine—



<sup>2</sup> Carbamic acid (p. 130) is amino formic acid.

<sup>3</sup> See note F at end of this chapter.

complex substances. Notwithstanding the difference in origin and in external appearance, they are very similar in composition, and have many properties in common. They are all classed together in one group, called albuminoids or proteins. The average composition of all these substances is—

Carbon . . . . .	52.2	per cent.
Hydrogen . . . . .	7.2	„ „
Oxygen . . . . .	23.1	„ „
Nitrogen . . . . .	15.8	„ „
Sulphur . . . . .	1.7	„ „
	<hr/>	
	100.0	

It is not yet known exactly how the elements are combined together, and their composition cannot therefore be indicated by formulæ. On exposure to air they become infected with bacteria, and are slowly decomposed, giving off offensive odours. In the process of digestion a somewhat similar series of changes occurs, and they can also be decomposed by chemical means. Amongst the most important compounds produced in all these changes are amines and amino-acid bodies, such as glycocoll, etc. It is believed, therefore, that the albuminoids or proteins are complexes of various amines and amino acids.

#### ADDITIONAL NOTES

A (p. 158). Acetylene burnt with excess of oxygen produces a flame of enormously high temperature, and oxy-acetylene blow-pipes are constructed giving a flame which can be used for piercing iron or even for cutting armour plate. It has a temperature of about 3300° C.

B (p. 162). Cadmium bromide and iodide are soluble in ether, and hence are used in the preparation of collodion photographic emulsions.

C (p. 167). The cleansing action of soap is largely due to its power of forming a lather, and this lather is caused by the fact that the solution of the soap in water lowers the surface tension of the liquid.

D (p. 175). Yeast contains several other enzymes besides zymase, each with a specific action which takes place most efficiently at a special temperature. Some, such as diastase, which is present

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in yeast, invert sugars ; some cause oxidation (oxydase), others reduce. Zymase is, however, as far as is known at present, the only yeast enzyme which produces alcohol.

E (p. 176). Saponin can also be extracted from horse-chestnuts, quillaia bark, and other vegetable products. It has a cleansing power similar to that of soap, and is of course unaffected by any hardness of the water. It is used in laundries to a small extent.

F (p. 184). Several important industrial applications have been found for casein. It is precipitated from skim milk either by dilute sulphuric acid or by passing sulphur dioxide through the liquid. The separated casein is then used :—

- (1) For sizing paper. For this purpose it is dissolved in ammonia ; water-glass is added to the solution, and then phosphoric acid or acetic acid.
- (2) As glue. For this it is mixed with a quarter of its weight of water and a little sodium bicarbonate.
- (3) As a food stuff.
- (4) For paints. It is mixed with about one-fifth of its weight of quicklime and the necessary colouring matter.
- (5) As artificial horn or ivory. The purified casein after being dried is treated with formalin and again dried ; it is then very hard and tough. It can be moulded when hot, and cut or turned on the lathe when cold.

## CHAPTER XV

### COAL TAR

THIS substance, which has already been mentioned as a by-product in the manufacture of coal gas (p. 121), is the most important source of a large number of carbon compounds many of which are of vast importance in the arts and industries, and also in medicine.

It is a very complex mixture. Upwards of 150 different compounds have been separated from it, and so great is the industrial value of the most important of them, that the coal tar is worth as much, if not more, than the coal gas which used to be the only material kept from the destructive distillation of coal.

The utilisation of coal tar and of the ammoniacal liquor obtained during this process provides, therefore, a convincing object lesson in the value of the study of bye-products and "waste" materials.

A ton of coal of high quality will produce about 10,000 cubic feet of coal gas, and somewhat more than 10 gallons of tar; also ammonia liquor sufficient for the preparation of about 30 lbs. of ammonium sulphate.

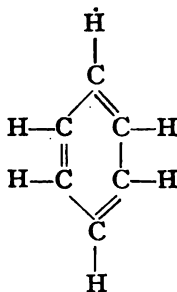
The coal tar is generally subjected to fractional distillation. The distillates are known commercially as (1) light oils (the distillate obtained below  $170^{\circ}\text{C.}$ ); (2) carbolic oils (between  $170^{\circ}$  and  $230^{\circ}$ ); (3) creosote oils ( $230^{\circ}$ – $270^{\circ}$ ); (4) anthracene oil (above  $270^{\circ}$ ). The residue is a black solid known as pitch.

Each of the oils can be further separated. From the light oils we obtain, by more careful distillation, a series of important

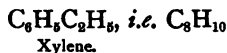
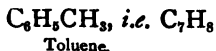


compounds, of which the most valuable, benzene, distils over in an almost pure condition.

This compound is the first of a series of hydrocarbons quite as important as the paraffins. It is represented by the formula  $C_6H_6$ , and various considerations determine that its constitution is best represented in the form of a ring—



By replacement of one of the hydrogen atoms by methyl, etc., other members of the series can be formed. The first three are—



The general formula for the series is  $C_nH_{2n-6}$ . It is known as the series of the aromatic hydrocarbons.

Benzene<sup>1</sup> is a colourless volatile liquid boiling at  $80.5^\circ \text{C}$ . Its odour is not unpleasant. It is highly inflammable, and burns with a luminous flame. It is largely used as a solvent of fats and oils, and is therefore employed in removing grease stains, etc.

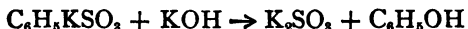
Benzene and its related hydrocarbons differ greatly in their properties from the paraffins.

The paraffins, for example, are not affected by concentrated sulphuric acid. If benzene, however, be treated with concentrated sulphuric acid, benzene sulphonic acid is formed—



<sup>1</sup> This must not be confused with benzine, which is a light *paraffin* oil. Benzene is often called Benzol.

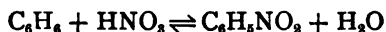
This substance forms salts with bases known as benzene-sulphonates. The potassium salt is  $C_6H_5KSO_3$ . When this salt is fused with caustic potash "carbolic acid" is produced—



"Carbolic acid" ( $C_6H_5OH$ ) is not really an acid; it is the mono hydroxyl derivative of benzene, more closely allied to alcohols than to acids. It is known as *phenol*.

Phenol is a colourless crystalline substance, soluble with difficulty in water, and miscible with alcohol and ether in all proportions. It has a peculiar characteristic odour, and is used largely as a disinfectant. Its poisonous properties, however, necessitate care in using it.

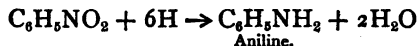
Again, the paraffins are not attacked by nitric acid, but benzene is nitrated. If benzene be mixed with concentrated sulphuric acid and nitric acid, and the mixture kept cool nitro benzene is formed—



(The sulphuric acid is added to remove water and prevent reversal of the reaction.)

Nitro-benzene, like most nitro-compounds, is yellow in colour. It is a liquid, boiling at  $205^\circ$ . It has an odour similar to that of bitter almonds, and is therefore sometimes used for imitating this odour, particularly in perfuming common soaps, etc. Commercially it is known as oil of mirbane.

Nitro-benzene is prepared on a large scale for conversion into aniline. This change is brought about by reduction, generally by nascent hydrogen—



Aniline is a colourless oily liquid which becomes brown on exposure to the air. It is slightly soluble in water, to which it imparts a faint alkaline reaction.

As will be seen from its formula, aniline has the same relation to benzene as ethyl amine has to ethane; it is, in fact, amino benzene. It forms salts with acids as the amines do. Aniline sulphate is  $C_6H_5NH_3HSO_4$ , and the acetate  $CH_3COOC_6H_5NH_2$ .

Like ammonium acetate, aniline acetate undergoes change on being gently heated, yielding acetanilide.<sup>1</sup>

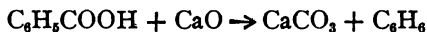


The second of the hydrocarbons, toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ , on being treated with chlorine gas in the presence of sunlight, yields, among other compounds, benzyl chloride,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ , and this, on being boiled for a long time with water, has its chlorine replaced by hydroxyl, forming  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ . The compound formed is benzyl alcohol.<sup>2</sup> On oxidation it yields an aldehyde called benzaldehyde, a compound which occurs in bitter almonds, laurel leaves, etc. Its formation from amygdalin is given on p. 175. Commercially, benzaldehyde (benzoic aldehyde) is made from bitter almonds. These may supply two per cent. of their weight, and owing to this method of preparation it is known as oil of bitter almonds. It is a liquid of a pleasant odour, scarcely soluble in water, and boiling at  $179^\circ \text{C}$ . It is not poisonous, and is used largely as a flavouring material.

Its formation from benzyl alcohol is expressed in the equation—



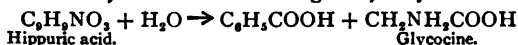
On exposure to the air benzaldehyde readily undergoes oxidation, forming benzoic acid,  $\text{C}_6\text{H}_5\text{COOH}$ . This compound occurs in gum benzoin, in Peru balsam and Tolu balsam, and, combined with glycocine (aminoacetic acid) in the urine of horses, cows, or other herbivorous animals.<sup>3</sup> Benzoic acid forms lustrous crystals which are fairly easily dissolved by hot water. When heated with lime or other alkali benzoic acid yields benzene—



<sup>1</sup> Acetanilide is used in medicine under the name of "Antifebrine."

<sup>2</sup> It will be remembered that a primary alcohol always contains the group  $\text{CH}_2\text{OH}$ . Benzyl alcohol is therefore a primary alcohol.

<sup>3</sup> The actual compound present is hippuric acid. This compound on being boiled with hydrochloric acid undergoes hydrolysis—

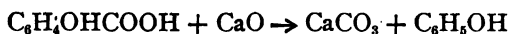


An important acid is obtained by causing the substitution of one of the hydrogen atoms of the group,  $C_6H_5$  (phenyl), by hydroxyl. The acid is  $C_6H_4OHCOOH$ , and is known as salicylic acid. It is found as the methyl ester in oil of winter-green, which owes its odour to the presence of this compound.

It can be prepared by treating phenol with carbon tetrachloride and alcoholic caustic potash, or more easily by treating the methyl salicylate obtained from oil of winter green with caustic potash.<sup>1</sup>

Salicylic acid is used as an antiseptic and as a food preservative.<sup>2</sup>

On being heated with lime or an alkali it yields phenol—



From the carbolic oils, the second distillate in the separation of coal tar, naphthalene can be obtained. This compound has the formula  $C_{10}H_8$ . It is largely used as an insecticide. It possesses a peculiar characteristic odour, and is a white crystalline solid, melting at about  $79^\circ C$ .

Many other compounds may be obtained from benzene, but they do not come within the scope of this work.

<sup>1</sup> The process of decomposing an ester with an alkali is known as saponification, from its analogy to the decomposition of fats by caustic alkalis and the resulting formation of soap.

<sup>2</sup> Salicylic acid is a drug with strongly marked properties, and therefore its use as a preservative cannot be recommended.

## CHAPTER XVI

### SOME COMMON METALS

THE term "metal" is applied to a large group of elements possessing those well-known and easily recognisable properties which are familiar to us in the case of silver, lead, gold, iron, etc. These properties are : a peculiar sheen, which for want of a more explanatory term is called a "metallic" lustre, malleability and ductility, or the capability of being hammered or rolled into thin leaves, and of being drawn into wire, and high conductive power towards heat and electricity.

The metals also generally form basic oxides, and can take the place of hydrogen in acids forming salts.

It may be convenient to divide the metals into two main groups as follows :—

I. Light metals, including—

- (a) The alkali metals : potassium, sodium, lithium, etc.
- (b) The metals of the alkaline earths : calcium, strontium, barium, and magnesium.
- (c) The earth metals : aluminium, and certain very rare elements.

II. Heavy metals (those with a specific gravity greater than 5), including—

- (a) The iron group : iron, manganese, nickel, cobalt, chromium, zinc, cadmium.
- (b) The copper group : copper, lead, mercury, silver.
- (c) The noble metals : gold and platinum.
- (d) Other metals : antimony, bismuth, tin, and possibly arsenic.

The scope of this book will not allow of a full description

of these elements. Some, however, are of such great importance that the student must become familiar with at least their most important properties.

**The Light Metals.**

(a) *The Alkali Metals.*—These form basic oxides soluble in water, *i.e.* alkalis.

*Sodium.*—This metal and its compounds have already been described (p. 80).

*Potassium.*—This element is very similar to sodium in most of its properties, but is more chemically active. Its more important compounds have already been described (p. 97).

(b) *The Metals of the Alkaline Earths.*—These metals form oxides of an earthy nature, slightly soluble in water, to which they impart an alkaline reaction.

*Calcium* (p. 65).

*Barium.*—The most plentiful minerals containing barium are barytes (heavy spar),  $\text{BaSO}_4$ , and witherite,  $\text{BaCO}_3$ . A solution of barium chloride,  $\text{BaCl}_2$ , is largely used in the laboratory as a test for sulphates, as barium sulphate is an extremely insoluble salt, and is therefore precipitated whenever barium chloride is added to the solution of a sulphate.

Barium sulphate is used in the preparation of permanent white paint, as it does not blacken in impure air. Barium peroxide is used in the commercial preparation of oxygen (p. 19).

*Magnesium.*—This metal is widely distributed in nature. It is found as magnesite,  $\text{MgCO}_3$ , and in larger quantities as dolomite or magnesian limestone,  $\text{MgCO}_3 \cdot \text{CaCO}_3$ . The sulphate and chloride are also found, and magnesium chloride and bromide occur in sea-water.

The metal is usually obtained by the electrolysis of fused carnallite,  $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ . It is white like silver, somewhat tough, and keeps fairly well in the air. It burns when heated, giving a light of great brilliancy and rich in chemically active rays, so that it is often used in photography. The compound formed on burning magnesium in air is chiefly oxide, but a small quantity of nitride,  $\text{Mg}_3\text{N}_2$ , is also produced (magnesium

combines directly with nitrogen). Magnesium acts invariably as a divalent element. It is rapidly acted upon by acids, forming the corresponding salt and liberating hydrogen. This is true, even in the case of nitric acid, if the acid be sufficiently dilute. When magnesium is dissolved in hydrochloric acid, the chloride is formed. This salt can be obtained in deliquescent crystals of the composition  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  from the solution. If, however, the crystals are heated, the salt undergoes hydrolysis, the oxide or a basic chloride being formed—



Magnesium sulphate is the substance well known as Epsom salts, it generally occurs crystallised with seven molecules of water of crystallisation,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ . Magnesium carbonate occurs in nature, but if an alkaline carbonate be added to a solution of a magnesium salt, a white precipitate is thrown down and carbon dioxide is liberated. This precipitate is no pure magnesium carbonate, but a mixture of carbonate and hydroxide in varying proportions. It is used in medicine after it has been washed and dried at a low temperature; it is known as “magnesia alba.” All the salts of magnesium, except the phosphate, are soluble in a solution of ammonium chloride, owing to the formation of double salts.

(c) *The Earth Metals*.—The only metal of this group which is at all common is aluminium.

*Aluminium* is one of the most plentiful elements in the crust of the earth; it is a constituent of most of the common rock-forming minerals.

The oxide of aluminium (alumina),  $\text{Al}_2\text{O}_3$ , is an earthy powder when prepared artificially, but occurs as a mineral in various forms. The commonest variety is emery or corundum, a substance only slightly less hard than the diamond. Ruby and sapphire are also aluminium oxide coloured with other metallic oxides.<sup>1</sup>

Aluminium oxide forms salts with acids, and also with strong

<sup>1</sup> In the ruby the colouring matter is a trace of chromium; while sapphire is coloured with cobalt.

bases (aluminates). The metal is soluble in hydrochloric and sulphuric acids, and in caustic soda or potash (p. 61).

When it is dissolved in sulphuric acid, aluminium sulphate is formed,  $\text{Al}_2(\text{SO}_4)_3$ . This sulphate forms important double salts with the sulphates of the alkalies, the most important being that with potassium sulphate. This is known as alum, and has the composition shown by the formula,  $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ . Several double salts of this nature are known, and the term "alum" is applied to them all. They contain the sulphate of a monovalent metal or of ammonia, and the sulphate of a trivalent metal, together with twenty-four molecules of water. They all crystallise in the same form, *i.e.* they are isomorphous.

The most important alums are—

- (1)  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Common alum.
- (2)  $\text{Na}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Sodium alum.
- (3)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Ammonium alum.
- (4)  $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Potassium chromium alum.
- (5)  $\text{Na}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Sodium chromium alum.
- (6)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Ammonium chromium alum.
- (7)  $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Potassium iron alum.
- (8)  $\text{Na}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Sodium iron alum.
- (9)  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ . Ammonium iron alum.

The sodium alums do not crystallise easily.

Aluminium salts are used as "mordants"<sup>1</sup> in dyeing. Their use is due to the fact that colloidal alumina combines with certain colouring matters to form insoluble coloured compounds. In dyeing, these compounds are formed in the fabric to be dyed, and as they are insoluble, the colour is fixed, *i.e.* not easily washed out. These insoluble compounds of a dye with a colloidal hydroxide are known as lakes.<sup>2</sup> The colour produced depends not only upon the dye, but also upon the mordant. Aluminium salts are also used in tanning leather.

<sup>1</sup> Lat. *mordere*, to bite. Salts of iron, chromium, and tin are used for a similar purpose.

<sup>2</sup> French, *laque*, lac.



The chief ore of aluminium is bauxite, which is chiefly alumina. From this ore the metal is obtained by electrolysis, the oxide being dissolved in fused cryolite,  $\text{Na}_3\text{AlF}_6$ .

Aluminium is a nearly white metal of low specific gravity (2.7); it keeps bright in dry air, but is quickly tarnished by water, especially by salt water. It is not acted on by nitric acid, nor by the vegetable acids. It can, therefore, be used for cooking utensils, but, if it is so used, care must be taken that alkalies such as soda are not brought into contact with it. It is also appreciably acted on by common salt.

**The Heavy Metals.**—(Sp. gr. over 5.)

*Iron.*—The chief compounds occurring in nature are the oxides,  $\text{Fe}_2\text{O}_3$ , hæmatite,  $\text{Fe}_3(\text{OH})_2$ , limonite,  $\text{Fe}_3\text{O}_4$ , magnetite (so called because many specimens of this mineral have magnetic properties),<sup>1</sup> and a carbonate  $\text{FeCO}_3$  (spathic iron ore). These constitute the ores of iron.<sup>2</sup> The carbonate of iron is often found mixed with clay, when the mineral is known as clay iron stone. It often contains organic material which makes it very dark in colour (black band iron stone).

The chemical process of obtaining iron from its ores (smelting) is a very simple one. Whatever form of ore is used, it is first turned into the oxide by roasting in the air; it is then reduced in a furnace, by carbon in the form of coke or small coal. The carbon removes the oxygen from the iron oxide, and forms large quantities of carbon monoxide. This gas, until comparatively recently, was allowed to escape and burn at the top of the blast furnace, but it is now led off and burned in a suitable "stove" in such a manner as to heat the air blast which passes into the furnace, thereby saving a large expenditure of fuel. As, however, many of the ores of iron contain impurities of a siliceous and infusible nature, limestone is always placed in the furnace with the iron ore and coal or coke. This combines with the siliceous material to form a fusible "slag" of a nature somewhat similar to glass. The metal when run out from the furnace is generally cast into

<sup>1</sup> It is the substance which was known as "lode stone."

<sup>2</sup> An *ore* is a naturally occurring compound which is used as a source of a metal.

bars about three feet long and six inches thick ; these are known as "pigs."

Iron is placed upon the market in three forms : wrought iron, cast iron, and steel. Of these, wrought iron is the purest. It is a dark grey metal with brilliant metallic lustre, and a specific gravity of 7.7. Its melting-point is extremely high (about  $1600^{\circ}\text{C}.$ ), but in order to work it, it is not necessary to raise its temperature to anything like this extent. Long before melting, wrought iron becomes soft almost like wax, and can in this condition (at about  $600^{\circ}\text{C}.$ ) be pressed, hammered, or rolled into any required shape. It can also be welded, that is, two pieces of the metal can be caused to unite when hammered or rolled together.<sup>1</sup>

Steel is iron which contains from 0.8 to 2.5 per cent. of carbon, in combination with the iron as iron carbide, but is otherwise as pure as can be produced. Wrought iron is tough and not very hard, and when heated and suddenly cooled these properties do not undergo any appreciable change ; but the presence of carbon in the iron greatly increases its hardness, and lowers its melting-point, so that steel is liquid at about  $1400^{\circ}\text{C}.$ , and can be cast. Steel, however, softens before it melts, and can, therefore, like wrought iron, be forged ; such treatment toughens the steel and causes it to become fibrous, whereas cast steel consists of fine crystalline grains. Continual knocking or vibration may cause forged steel to revert to its crystalline condition and become brittle.<sup>2</sup>

A most important property of steel is its power of being tempered, or rendered soft or hard at will. In order to make steel assume any required degree of hardness, it is first of all made red hot, and then cooled suddenly by plunging it into cold water or mercury. With the latter material it becomes so hard that it will cut glass—it is said to be "glass hardened."

<sup>1</sup> A few other metals possess the property of welding, the chief being platinum, which can be welded at a red heat, and gold, which can be welded even when cold. Lead may also be included among the weldable metals.

<sup>2</sup> The axles of railway carriage wheels have been known to break after much use, owing to this change in structure.

The metal is then put upon a "hot plate" and carefully heated. As heated iron oxidises readily in the air, a film of oxide is soon formed on the surface. This varies in colour with its thickness, first appearing as a pale straw colour at about  $220^{\circ}\text{C}$ ., and then passing through various shades of orange, purple, violet, and blue, to grey. The higher the temperature to which the hardened steel is heated the softer it becomes. A skilful workman can tell by the colour of the metal approximately what temperature has been reached, and can stop the heating when the desired condition has been attained. Thus tools for steel engraving are only allowed to reach the straw-coloured stage (about  $221^{\circ}\text{C}$ .), while springs and wood saws are heated until the colour of the film of oxide is almost grey (just below  $300^{\circ}\text{C}$ .).

In the manufacture of steel from iron containing phosphorus, the converter is lined with a mixture containing lime and magnesia, which absorbs the phosphoric oxide produced during the process, and forms basic calcium phosphate. When the lining has absorbed all the phosphorus it can take up, it is removed, and when pulverised is sold as a phosphatic fertiliser. It is called "basic slag." It is not, however, a slag in the usual sense, as it is not a fusible material.

If the amount of carbon is increased to 4 or 5 per cent., the melting-point of the metal becomes still lower; the metal also loses its toughness and is crystalline and somewhat brittle. It is now known as *cast iron*. There are two kinds of cast iron, grey and white.

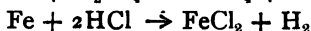
White cast iron has the greater part of its carbon combined with the iron, it is obtained by rapidly cooling the melted metal. On slowly cooling, some of the carbon separates as minute crystals of graphite, which impart a grey colour to the metal.

All kinds of iron oxidise readily in moist air, even at ordinary temperatures, forming impure  $\text{Fe}(\text{OH})_3$  (iron rust). When heated strongly, oxidation quickly takes place, and the compounds  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  are produced.

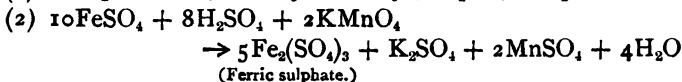
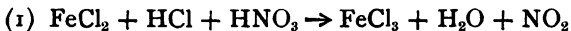
Owing to the rusting of iron in moist air at a low temperature, and to the fact that the rust formed does not adhere to

the metal, it is necessary to protect the iron from the action of the atmosphere. This is often done by covering it with a coating of paint, or it is galvanised (p. 204), tinned (p. 212), or nickel-plated (p. 203). For a similar protective purpose, iron which has to be heated is often covered with a coating of black lead (graphite).

When iron is treated with dilute sulphuric or hydrochloric acid, hydrogen is evolved,<sup>1</sup> and a salt of iron formed in which one atom of iron takes the place of two atoms of hydrogen.



Such salts are known as *ferrous* salts. They form green crystals containing water of crystallisation. Ferrous sulphate is the most familiar of these; it has been known for a very long time under the names of green vitriol, copperas, etc., and has been largely used in the making of writing ink.<sup>2</sup> When exposed to the air, the ferrous salts are slowly oxidised, a change which can be brought about more quickly by the action of an oxidising agent such as nitric acid or potassium permanganate.



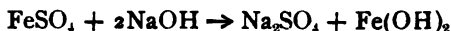
In these reactions the salts  $\text{FeCl}_3$  and  $\text{Fe}_2(\text{SO}_4)_3$  are formed, and in them the iron is obviously trivalent. They are known as *ferric* salts. Ferric salts are usually yellow in colour,<sup>3</sup> so that the oxidation of the ferrous salt by nitric acid is accompanied by a change in the colour of the solution from green to yellow or brown.

<sup>1</sup> The hydrogen thus obtained is always impure, owing to the presence of compounds of carbon and hydrogen formed by the action of the acid upon the iron carbide contained in the metal.

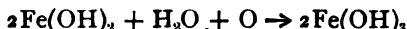
<sup>2</sup> Ink is formed from ferrous sulphate by adding a solution of gallic acid to a solution of the salt. It is owing to the iron that ink contains that ink stains on linen often develop into the rusty-brown marks known as "iron-mould." These consist of deposits of ferric oxide in the fibres of the material. Ink stains can be removed by a solution of oxalic acid or "Salts of Sorrel" ( $\text{KHC}_2\text{O}_4$ ).

<sup>3</sup> Iron alum, which is a ferric salt, forms pale violet crystals.

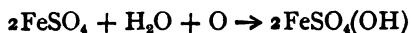
If a solution of caustic soda or potash or of ammonia be added to a solution of a ferrous salt a greenish precipitate is produced which rapidly turns brown on exposure to the air. If a perfectly pure ferrous salt be used, and the precipitation carried out in the absence of air, the solid thrown down is nearly white; it is ferrous hydroxide—



The oxidation to  $\text{Fe(OH)}_3$  causing the brown colour may be represented thus—



Ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (green vitriol) was used for preparing fuming sulphuric acid. For this purpose the salt was first roasted in the air, whereby it became converted into basic ferric sulphate—



and this on being heated decomposed—



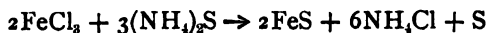
and the resulting mixture of sulphuric acid and sulphur trioxide was collected and sold as fuming oil of vitriol (p. 91).

Iron combines with sulphur when heated (p. 3), forming ferrous sulphide. This compound can also be obtained by adding ammonium sulphide to a solution of an iron salt.

(i.) Ferrous salt—



(ii.) Ferric salt—



The sulphide  $\text{Fe}_2\text{S}_3$ , corresponding to the oxide  $\text{Fe}_2\text{O}_3$ , is not known.

The following are some of the chief compounds of iron in common use :—

Ferric oxide,  $\text{Fe}_2\text{O}_3$ . Polishing material,<sup>1</sup> jewellers' rouge.  
Colouring material, Venetian red.

<sup>1</sup> Ferric oxide was known to the later alchemists as "Crocus Martis," as the element iron was generally referred to by the name of Mars, with which planet it was supposed to be very closely connected.

Ferric hydroxide,  $\text{Fe}(\text{OH})_3$ . Pigment (Mars orange, etc.).

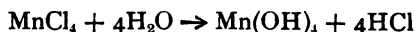
Also used as an antidote in cases of arsenical poisoning.

Ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . (Green vitriol.) Used in the making of writing ink (p. 199, note).

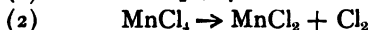
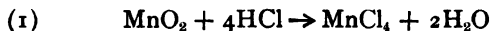
Ferric ferrocyanide,  $\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_6]_3$ . Used as a pigment under the name of Prussian blue.

*Manganese*.—This is a reddish-grey, lustrous metal, obtained from its oxide by reduction with aluminium. It melts at a higher temperature than iron, and is readily dissolved by acids, even acetic acid, with evolution of hydrogen and formation manganous salts. These salts are generally crystalline substances, pink in colour.

One of the most familiar compounds of manganese is the dioxide  $\text{MnO}_2$ , which occurs as a natural mineral and is then known as pyrolusite. Manganese dioxide will dissolve in cold concentrated hydrochloric acid without evolution of chlorine (p. 79), forming a dark brown-green liquid. If water be added to this liquid the hydrated dioxide is again thrown down. This is due to the formation of a tetrachloride ( $\text{MnCl}_4$ ), which is decomposed by water (hydrolysed)—



If the dark brown-green solution be boiled it rapidly becomes nearly colourless and loses chlorine. The reaction for the preparation of chlorine in this manner may be therefore represented as taking place in two stages—



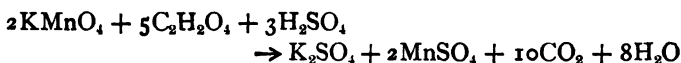
There are several oxides of manganese:  $\text{MnO}$ , obtained as the hydrate ( $\text{Mn}(\text{OH})_2$ ) by adding an alkali (caustic soda) to a manganous salt;  $\text{Mn}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_4$ ,  $\text{MnO}_2$ ,  $\text{Mn}_2\text{O}_7$ , and  $\text{Mn}_2\text{O}_7$ . Of these  $\text{MnO}$  and  $\text{Mn}_2\text{O}_3$  are basic oxides, the former giving rise to manganous salts and the latter to manganic salts.<sup>1</sup> The oxides  $\text{MnO}_3$  and  $\text{Mn}_2\text{O}_7$  are acidic and give rise to salts known as manganates and permanganates.

The soluble manganates are green, the permanganates are

<sup>1</sup> Manganic salts are unstable in the presence of water.

bright violet in solution. The most familiar permanganates are those of sodium and potassium. They are powerful oxidising agents and are used as disinfectants, the solution of sodium permanganate,  $\text{NaMnO}_4$ , being largely sold under the name of "Condy's Fluid."

The oxidising power of permanganates is utilised in many ways. A very important application in the chemical laboratory is the estimation of ferrous salts (p. 199), oxalic acid, hydrogen peroxide, etc. In all these cases the oxidation is made to take place in the presence of sulphuric acid, and the permanganate is reduced to a manganous salt—



In the presence of sulphuric acid five-eighths of the oxygen in a permanganate is available for oxidation.

Manganese dioxide,  $\text{MnO}_2$ , may also act as a weak acidic oxide, and a compound  $\text{CaMnO}_3$  is formed from the manganous chloride left after the preparation of chlorine, as a means of recovering the manganese dioxide, for this compound (calcium manganite) will liberate chlorine from hydrochloric acid—



Manganese dioxide is also used in colouring porcelain. Alone, it imparts a violet tint; in the presence of a little iron the colour obtained is brown. In the manufacture of glass it is also added to remove the green tint which would be imparted by small quantities of ferrous iron. This it does partly by oxidising the iron to the ferric condition. Ferric salts would colour the glass yellow, but the colour is much feebler than the green imparted by ferrous salts, and therefore the glass is left almost colourless. Moreover, any yellow colour is counteracted by the violet which the manganese would give alone, an imperceptible neutral tint being produced. Glass thus decolorised with manganese slowly turns violet on exposure to bright sunlight.

In addition to the manganese compounds already enumerated, manganese borate is of some importance. It is placed on the market as a brown powder and is used in the preparation of varnish, as a very small quantity added to linseed oil (p. 166) causes the oil to absorb oxygen, resinise, and to harden much more rapidly.

*Nickel*.—The metal is familiar, as it is often used as a protective covering for iron, upon which it is deposited by the electric current. The iron is then said to be nickel plated. The alloy of nickel with zinc and copper is known as German silver.

The nickelous salts are apple green in colour when crystallised; the commonest is the sulphate,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ .

*Cobalt*.—This metal is similar to nickel in its chemical properties. Its oxide,  $\text{CoO}$ , is chiefly used in colouring glass, to which it imparts a fine blue colour. Various blue pigments (smalt, cobalt blue, etc.) are silicates of a glassy nature, reduced to a very fine powder.

Cobaltous salts are pink when they contain water of crystallisation, but are blue when anhydrous.

*Chromium*.—A metal which has received its name from the variety of colours which its compounds display.

Chromium itself is a bright, pale grey, very hard metal, of very great infusibility (it melts at a temperature of about  $3000^\circ\text{C}$ ). It is dissolved by hydrochloric acid and sulphuric acid, and assumes the passive state<sup>1</sup> when treated with concentrated nitric acid.

It forms chromic salts in which the metal is trivalent (chromic sulphate is  $\text{Cr}_2(\text{SO}_4)_3$ ); these salts are either green or violet (chrome alum, p. 195); and chromous salts in which it is divalent. Chromous chloride,  $\text{CrCl}_2$ , is bright blue in colour; chromous acetate is chocolate red.

Chromium also forms an acidic oxide,  $\text{CrO}_3$ , which yields,

<sup>1</sup> The "passive" state is also assumed by iron. Both iron and chromium after being dipped in very concentrated nitric acid, no longer dissolve in acids. This change in properties is supposed to be due to the formation of a thin coating of difficultly soluble oxide. A sharp blow causes the metal to resume its active condition, not only at the point where it is struck, but over the entire surface.



with water, chromic acid,  $\text{H}_2\text{CrO}_4$ . The salts are known as chromates and are either yellow or red; they are powerful oxidising agents. Potassium chromate,  $\text{K}_2\text{CrO}_4$ , and potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$ , *i.e.*  $\text{K}_2\text{CrO}_4 \cdot \text{CrO}_3$ , are perhaps the most important.

Chromic oxide,  $\text{Cr}_2\text{O}_3$ , is a green substance largely used as a pigment.

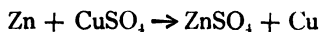
*Zinc.*—This metal occurs in nature as sulphide,  $\text{ZnS}$  (zincblende), and also as carbonate (calamine) and silicate.

It is a pale grey, somewhat soft metal which melts at  $420^\circ\text{C}$ . It is largely used not only in a pure state but also in many alloys (p. 216). It finds an important application in art castings, as it is fairly cheap, and can easily be coloured externally to look like bronze.

It is also used for coating iron plates, which are then known as "galvanised" iron; this name arose from the fact that the zinc was originally deposited upon the iron by an electric current; now, however, the iron plates are merely dipped in molten zinc. Zinc-covered iron should not be used for drinking vessels, as the zinc is somewhat easily attacked by moist air, and the compounds formed are poisonous.

Zinc as fine turnings or thin foil burns in the air with a bluish-green flame forming zinc oxide

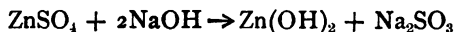
It forms but one series of salts and in these it is divalent. Many of them can be obtained by dissolving the metal in the corresponding acid, when hydrogen is liberated and the salt produced. If zinc is absolutely pure, it is almost insoluble in acids. Contact with a small piece of another metal such as platinum or copper, however, causes the solution of the zinc with the liberation of hydrogen at the surface of the other metal. The same effect may be brought about by adding a small quantity of a solution of a salt of silver, copper, or lead. In this case the zinc replaces the metal in its salt—



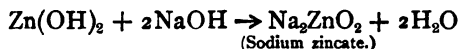
thereby bringing the zinc in contact with metallic copper or other metal.

Zinc oxide can be obtained from the salts of zinc by the

addition of the solution of an alkali. A white flocculent precipitate is thrown down ; this is zinc hydroxide—



If the zinc hydroxide be filtered off, washed and heated strongly, it loses its water and becomes converted into zinc oxide. Should, however, an excess of caustic alkali be added, the precipitate of zinc hydroxide dissolves. This is due to the formation of a soluble salt in which the zinc oxide acts in an acidic manner.



Zinc oxide is often used as a white pigment under the name of zinc white ; it is also used in medicine.

Precipitated zinc sulphide, which is also white, is similarly used in the preparation of white paints. It is obtained when ammonium sulphide is added to a solution of a zinc salt.

Zinc sulphate (white vitriol),  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , is a white crystalline salt easily soluble in water.

*Cadmium.*—A metal very similar to zinc in its chemical properties, and often found in small quantities in zinc ores. It is a pale bluish-grey metal nearly as soft as lead.

Cadmium sulphide,  $\text{CaS}$ , is used as a pigment under the name of cadmium yellow.

*Copper.*—This is, industrially, one of the most important of the metallic elements. It occurs native, and for this reason, it has, together with gold and silver, been known from a very early period. It is characterised by its bright rose-red colour. This colour is, however, only seen in fresh surfaces, for in a short time the metal becomes covered with a film of oxygen or sulphur compounds, which, without at first destroying the metallic lustre, impart to the metal the brown-red colour usually known as “copper-red.”

The chief compounds of copper which occur in nature are copper pyrites,  $\text{CuFeS}_2$ , malachite (a basic carbonate of copper),  $\text{Cu}(\text{OH})_2\text{CuCO}_3$ , and cuprite or ruby copper ore,  $\text{Cu}_2\text{O}$ .

The metal has a specific gravity of 8·8 ; it is tough, tenacious, malleable, and ductile.

It is largely used for utensils of all kinds, and owing to the fact that it can be beaten into any required shape it finds application for ornamental and artistic purposes.

It is also occasionally used for roofing, although when exposed to moist air it gradually becomes covered with a green layer consisting of oxygen compounds and basic carbonate, which, however, never becomes very thick.

Its high conductivity for the electric current—it is inferior to silver only in this respect—causes it to be extensively used in electrical engineering. Telephone and telegraph wires are invariably made of it.

When copper is heated to a red heat it combines fairly rapidly with oxygen, the oxide forming black scales on the metal, which fall off and leave a fresh surface for oxidation.

Copper is not easily attacked by any dilute acid with the exception of nitric acid. Hot concentrated sulphuric acid dissolves it (p. 86). Nitric acid readily attacks it, the gaseous products of the reaction varying with the strength of the acid (p. 136).

Copper forms two basic oxides and two series of salts, *cupric* and *cuprous*, of which the cupric are the more stable under ordinary conditions. In these, the copper is divalent, while in the cuprous salts it is probably monovalent.

When copper is dissolved in nitric acid, a blue solution is formed which on evaporation at a moderate temperature leaves blue crystals of cupric nitrate,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ .

If to a solution of copper nitrate caustic soda is added, a bright blue gelatinous precipitate is thrown down; this is cupric hydroxide,  $\text{Cu}(\text{OH})_2$ . On boiling, the precipitate loses water and also its blue colour, being converted into a heavy black precipitate of cupric oxide,  $\text{CuO}$ . If the hydroxide or oxide be treated with other acids the corresponding cupric salt is formed.

The most important cupric salts are :—

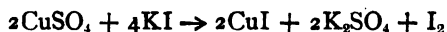
(1) Cupric sulphate,  $\text{CuSO}_4$ . This compound when anhydrous is a yellowish white solid, but it is more often seen combined with water as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (blue stone or blue vitriol). This salt has a limited application in agriculture.

Bordeaux mixture, used as a fungicide, is made by mixing copper sulphate with slaked lime.

(2) Cupric chloride,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , can be obtained as blue crystals, the anhydrous salt is yellow.

*Cuprous Salts.*—If cupric chloride be boiled with copper and concentrated hydrochloric acid, a dark liquid is obtained, which on being poured into water throws down white crystals of cuprous chloride,  $\text{CuCl}$ . The same compound is obtained when sulphur dioxide is passed into a solution of cupric chloride. Cuprous chloride is insoluble in water and is readily oxidised to a cupric compound on exposure to the air.

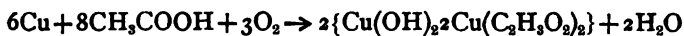
If, again, a solution of potassium iodide be added to a solution of a cupric salt, *cuprous* iodide is obtained as a white precipitate, coloured brown by liberated iodine—



Cuprous oxide is easily obtained by treating a cuprous salt with a caustic alkali, but the student is more likely to become acquainted with it in testing for glucose (p. 171).

Other compounds of copper which are of importance are—

(1) Cupric acetate: this salt can be obtained in blue-green crystals by dissolving cupric hydroxide in acetic acid and crystallising the solution. If, however, copper is exposed to the air in contact with dilute acetic acid, basic cupric acetate is formed—



This compound is known as verdigris.

By treating it with arsenious acid and acetic acid

(2) Cupric arsenio-acetate is produced as a light-green solid of peculiarly brilliant tint. This is Paris green or emerald green; it is largely used as a pigment.

Its formula is  $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2\text{Cu}_3\text{As}_2\text{O}_6$ .

(3) Scheele's green is  $\text{CuHAsO}_3$ ; it has been used as a green pigment, but the poisonous nature of this and emerald green limit their use considerably. Both of the materials, however, are used occasionally as fungicides and insecticides.

Cupric salts can easily be detected in solution by the deep

blue colour produced by ammonia, due to a compound of the copper salt and the ammonia. Thus copper sulphate forms  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ , which can be obtained from the solution by addition of alcohol, in which it is insoluble. These deep blue compounds have the power of dissolving cellulose, and their solutions have been used for "water-proofing" paper.

Towards both animal and vegetable life, copper salts generally act as powerful poisons.

**Lead.**—This is another metal of high industrial importance. It is found in nature chiefly as sulphide, ( $\text{PbS}$ ), galena, and as carbonate ( $\text{PbCO}_3$ ), cerussite.

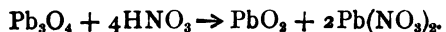
The many uses of the metal depend chiefly upon its low melting-point,  $326^\circ \text{C}$ ., its great density (sp. gr. 11.4), and its softness. It is used either alone or alloyed with other metals (p. 216). Sheet lead is used for roofing; lead foil forms an airtight package for tea, and lead pipes are often employed to carry the water supply to houses. There is, however, some danger in the use of lead water-pipes, unless the water be hard. Hard water will generally cover lead with a coating of carbonate which is insoluble, and which protects the metal from further action. Soft water, however, containing little or no carbonate but having oxygen in solution, causes the formation of lead hydroxide which is perceptibly soluble. Lead thus dissolved in water acts as a powerful poison. Cases of lead poisoning produced by water which has passed through lead pipes are not uncommon. The danger is removed by coating the inside of the pipes with tin. Lead forms a series of oxides. They are  $\text{Pb}_2\text{O}$ ,  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{Pb}_2\text{O}_3$ ,  $\text{PbO}_2$ . Of these the most important are the following:—

**Lead Monoxide,  $\text{PbO}$ .**—This is prepared in two forms; a yellowish-red crystalline substance obtained by direct oxidation of lead, known as litharge; a yellow powdery variety made by heating lead nitrate or carbonate,<sup>1</sup> known as massicot. Lead monoxide is used in glass-making, for preparing salts of lead, and in the manufacture of drying oils.

<sup>1</sup> All the other oxides of lead are converted into massicot on being heated strongly in the air.

It is a basic oxide, but can act as a feeble acidic oxide with strong bases.

**Red Lead**, Minium,  $Pb_3O_4$ , may be formed by carefully heating litharge in the air. It is a substance of a bright red colour, and has been employed for a very long time as a pigment.<sup>1</sup> When treated with nitric acid it yields lead peroxide and lead nitrate.



**Lead Peroxide**,  $PbO_2$ .—A dark-brown powder which readily evolves oxygen on heating.

The salts of lead are generally insoluble in water, the chief exceptions being the acetate and the nitrate. The acetate has an extensive industrial use. It has a sweet taste (it is very poisonous), and is therefore known as sugar of lead.

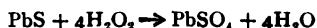
**White Lead** is a mixture of basic carbonates. It is prepared by the action of carbon dioxide upon lead oxide. Several methods are employed, the most common at the present time is that of grinding lead oxide with lead acetate and water and passing carbon dioxide through the mixture.

It is largely used for making white paint; it has a great advantage over all other white paints in its much greater opacity and covering power. The disadvantages attending its use have, however, led to the substitution of other white materials ( $ZnO$ ,  $ZnS$ ,  $BaSO_4$ , etc.), for all lead compounds very readily turn black in air containing traces of sulphuretted hydrogen, the blackening being caused by the formation of lead sulphide,  $PbS$ .<sup>2</sup>

**Lead Chromate**,  $PbCrO_4$ , is used as a yellow pigment under the name of chrome yellow. On being warmed with caustic soda a basic lead chromate is formed, which is of a dark orange tint and is known as chrome red. Various mixtures of these

<sup>1</sup> Red-lead mixed with linseed oil, etc., is used in making gas-tight joints with gas pipes. The substance assists the resinisation of the oil.

<sup>2</sup> Paint which has been blackened in this manner can generally be made white again by the application of hydrogen peroxide, which oxidises the sulphide to sulphate—



two compounds are employed to give different tints of orange and yellow. The chrome yellow is easily prepared by adding potassium chromate or bichromate to a solution of lead acetate in water.

**Mercury.**—This is the only metal which is liquid at the ordinary temperature. It is largely employed in making barometers, thermometers, and other scientific instruments. It is a bright, lustrous metal of great density (sp. gr. 13.59), and boils at a temperature of  $358^{\circ}\text{C}$ . It remains untarnished in the air at ordinary temperature indefinitely, but if heated for a long time to about  $300^{\circ}\text{C}$  it becomes covered with red scales of mercuric oxide (p. 15).

The most important compounds of mercury are *mercuric sulphide* ( $\text{HgS}$ ). This forms the commonest ore of mercury, cinnabar. Artificially prepared, mercuric sulphide is the red pigment known as vermilion.<sup>1</sup> *Mercurous chloride*,  $\text{HgCl}$ , long known under the name of calomel,<sup>2</sup> is used to some extent in medicine. *Mercuric chloride*,  $\text{HgCl}_2$ , is used as an antiseptic. It is known as corrosive sublimate. All the salts of mercury are poisonous.

Mercury forms alloys, known as amalgams, with many metals, some of which have industrial application.

**Silver.**—This metal has been known from the earliest times, as it occurs free in nature. This and the manner in which it resists oxidation in the air either cold or when heated, its fine whiteness, and its brilliant lustre when polished, have caused it to be used in all ages for articles of ornament and for coinage. It melts at about  $945^{\circ}\text{C}$ ., and although oxygen does not combine with it at ordinary pressure even when the silver is melted, yet the metal absorbs this gas to the extent of about twenty-two times its own volume, and, on solidifying, gives it out again, so that the surface of silver which has been melted

<sup>1</sup> When sulphuretted hydrogen is passed through a solution of a mercuric salt a *black* precipitate of mercuric sulphide is thrown down; on treatment with a solution of an alkali sulphide the black precipitate gradually turns red, owing to the formation of the crystalline red form of mercuric sulphide.

<sup>2</sup> Gk. *καλός*, beautiful; *μέλας*, black. It forms a black substance with ammonia. This substance contains free mercury.

and cooled is always pitted with apertures from which the oxygen has escaped.

Silver is not attacked by dilute acids except nitric acid, but this easily dissolves it, forming silver nitrate. Concentrated sulphuric acid also dissolves it, forming silver sulphate and liberating sulphur dioxide. The metal is easily acted upon by sulphuretted hydrogen and many other sulphur compounds. Thus silver spoons become blackened from contact with the albumen of egg (this contains sulphur), and silver articles in the pocket will, if in contact with indiarubber or vulcanite, such as the handle of a fountain-pen, become black from the sulphur which these materials contain. In all cases the blackening is caused by the formation of a film of silver sulphide,  $\text{Ag}_2\text{S}$ .

Silver forms but one series of salts in which it is monovalent. That most easily obtained is the nitrate, which readily crystallises in anhydrous crystals from the solution obtained by dissolving silver in nitric acid. The salt is often fused and cast in sticks for medical use, as it acts as a strong caustic. It often goes by the name of "Lunar caustic," from "*Luna*," the moon, the name applied to silver by the mediæval alchemists.

From the solution of the nitrate, soluble chlorides precipitate the very insoluble white silver chloride,  $\text{AgCl}$ . This salt, together with the bromide and iodide, has wide application in photography, owing to the fact that light causes a change in its colour. Under the influence of light, silver chloride slowly becomes violet in tint. All silver salts are more or less affected by light in this way, the change being greatly assisted by the presence of traces of oxidisable matter. Most of the salts of silver are soluble in ammonia solution.

**The Noble Metals.**—Gold and platinum are remarkable for the fact that they occur in nature almost entirely in the native condition. Both are unacted upon by all acids except the mixture of hydrochloric and nitric acids known as aqua regia (p. 80). This dissolves them and forms the chlorides.

Gold has for ages been used for personal ornament and for coinage. It is a heavy soft yellow metal (sp. gr. 19.3); it melts at  $1035^\circ\text{C}$ . Its malleability is remarkable; it may be



rolled or beaten out into leaves so thin as to transmit light (the light so transmitted is greenish). These leaves are used under the name of gold-leaf for surface decoration.

As gold is so soft, it is usually alloyed with copper for both jewellery and coinage, and is thereby rendered somewhat more red in tint. Coinage from the Australian mint at Sydney is, however, alloyed with silver, and is therefore of a very pale yellow colour. The only salt of importance is the chloride,  $\text{AuCl}_3$ ; on being heated it loses its chlorine and leaves metallic gold.

Platinum chloride,  $\text{PtCl}_4$ , decomposes in the same way and leaves platinum in the form of a black powder known as platinum sponge (p. 88). Platinum chloride has an important application in the estimation of the element potassium, a double chloride of potassium and platinum being formed when the salts are mixed. This double chloride is insoluble in alcohol.

The metal may be easily precipitated from the solutions of its salts by reducing agents such as formic acid.

The high melting point of platinum (about  $1770^\circ\text{C}.$ ), its malleability and ductility, and its resistance to the action of all acids render it of very great use in chemistry and in many industries; its scarcity is a matter for regret.

**Antimony** is a metallic-looking substance of specific gravity 6.7, and melts at  $40^\circ\text{C}.$  It is very brittle, and can easily be broken and ground to a fine powder. It shows a strong tendency to form acidic oxides. Its compounds are poisonous.

**Bismuth** is a brittle metal. Its colour is grey with a slightly red tinge. The basic nitrate is used in medicine as "subnitrate" of bismuth.

**Tin.**—A white crystalline metal of great malleability. Tin foil is largely used as an ornamental and air-tight packing material. Sometimes, if kept at a low temperature, tin slowly changes into a grey powdery modification. It does not oxidise in the air, and is therefore employed for protecting iron, plates of this metal being dipped into molten tin. The tin-covered iron is known as "tin-plate," and all the various forms of canisters, commonly known as "tins," are made

from it.<sup>1</sup> Copper vessels are sometimes coated with it, as are also common pins.

Tin is attacked by hydrochloric acid; stannous chloride,  $\text{SnCl}_2$ , is formed and hydrogen is liberated. Stannous chloride is known commercially as tin salt, and is used as a "mordant" in dyeing. The action of chlorine gas upon tin leads to the formation of the liquid stannic chloride,  $\text{SnCl}_4$ . The metal is also attacked by nitric acid, the cold dilute acid giving stannous nitrate—



Concentrated nitric acid yields stannic nitrate, which is, however, at the temperature of the reaction, decomposed by water, yielding metastannic acid,  $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ .



On heating the white solid metastannic acid, a straw-coloured powder of stannic oxide,  $\text{SnO}_2$ , is left.

Tin forms two sulphides, stannous sulphide ( $\text{SnS}$ ), which is thrown down as a brown precipitate when sulphuretted hydrogen is passed through a solution of a stannous salt, and stannic sulphide,  $\text{SnS}_2$ , can be obtained as a yellow precipitate from stannic salts in the same manner. Stannic sulphide is also made by heating together tin filings, sulphur, ammonium chloride, and mercury; the ammonium chloride and the mercury are volatilised, and stannic sulphide is left as a brilliant yellow crystalline solid. It is used in jewellery and enamel work as "Mosaic gold," also as a "Bronze powder."

The oxide,  $\text{SnO}_2$ , is used in pottery for the preparation of a white enamel.

**Arsenic.**—The element arsenic possesses so few of the metallic properties, that it is generally classed among the non-metals. It is closely related to phosphorus in most of its chemical properties. In its most common form it is a dark grey crystalline substance with a metallic lustre. At ordinary pressure it does not melt, but on being heated passes at once

<sup>1</sup> Tin is not attacked by water, and iron vessels protected with this metal can therefore be safely used as drinking-vessels, or for holding milk.

into a brownish-yellow vapour. Various allotropic forms are known.

When arsenic is heated in presence of oxygen it burns with a brilliant white flame, forming an oxide,  $\text{As}_4\text{O}_6$ . This is generally referred to as arsenic trioxide; its formula is sometimes given as  $\text{As}_2\text{O}_3$ , but the density of the vapour is 198, which corresponds to a molecular weight of 396, and this agrees with the formula first written.

This oxide is the commonest compound of arsenic, and is usually known as "White Arsenic." It is an acidic oxide which dissolves in alkalis and in alkaline carbonates, forming arsenites—



When manufactured on a large scale, it first appears as a transparent glassy material (amorphous), which, on keeping, gradually becomes white and opaque like porcelain (crystalline).

All the compounds of arsenic are extremely poisonous, and many of them are characterised by an objectionable garlic-like odour.

If white arsenic be treated with nitric acid, arsenic acid,  $\text{H}_3\text{AsO}_4$ , crystallises out. This acid is in many respects similar to orthophosphoric acid, and its salts yield a yellow precipitate with ammonium molybdate.\* When heated, arsenic acid loses water and leaves the pentoxide, which, on being more strongly heated, decomposes into oxygen and  $\text{As}_4\text{O}_6$ .

Arsenic combines with hydrogen, forming the hydride  $\text{AsH}_3$  (arsenietted hydrogen), an extremely poisonous gas, which is produced whenever hydrogen is liberated in the presence of arsenic or its compounds.

The liberation of the gas forms a very delicate test for arsenic. If, for instance, hydrogen be liberated from zinc and dilute sulphuric acid, and a very small quantity of an arsenic compound placed in the apparatus with the mixture, arsenietted hydrogen,  $\text{AsH}_3$ , is evolved with the hydrogen, and if the gas is passed through a hard glass tube heated at one point, the

\* Ammonium molybdate also gives a yellow precipitate with phosphates in nitric acid solution.

presence of the arsenic is shown by the formation of a black mirror-like deposit. This deposit is arsenic formed by the decomposition of the hydride. Antimony hydride,  $\text{SbH}_3$ , can be prepared in a similar manner, and it behaves in the same way, but the deposits may be distinguished by the solubility of the arsenic mirror in sodium hypochlorite. A more simple way of showing the presence of arsenic hydride, and therefore of arsenic, is to liberate hydrogen as described above, adding the substance suspected of containing arsenic, and to burn the gas at a jet. On holding a piece of cold porcelain in the flame a black lustrous deposit of arsenic is obtained.

Arsenic is precipitated from its solutions by sulphuretted hydrogen as a yellow sulphide,  $\text{As}_2\text{S}_3$ , soluble in solutions of alkalis or of alkaline sulphides, also in a solution of ammonium carbonate.

## SOME IMPORTANT ALLOYS, WITH THEIR APPROXIMATE COMPOSITION.

	Per cent.	
Aluminium bronze .	Copper . 90 Aluminium 10	A bright gold-coloured alloy, hard and tenacious.
Gun metal . . . .	Copper . 90 Tin . . . 10	Reddish-yellow metal, tough and tenacious. It is the material of which large guns were formerly cast.
Bell metal . . . .	Copper . 78 Tin . . . 22	Yellowish-grey alloy, hard, brittle, and very sonorous.
Brass (many varieties of this alloy are made)	Copper . 71.4 Zinc . . 28.6	This is the composition of ordinary brass. It is a pale yellow alloy.
	Copper . 60 Zinc . . 40	This is the alloy known as Muntz metal.
Bronze . . . . .	Copper . 88 Tin . . . 9 Zinc . . 2 Lead . . 1	This is one of the bronzes used for statuary. Some bronzes contain copper and tin only.
German silver . . .	Copper . 50 Nickel . 26 Zinc . . 24	A white alloy. A good imitation of silver. German silver is sometimes made without zinc.
Pewter . . . . .	Tin . . . 90 Antimony . 7 Bismuth . 2 Copper . 1	A pale grey alloy taking a high polish.
Solder (soft) . . .	Lead . . 33.3 Tin . . . 66.6	Many solders are made, suitable for various purposes.
Type metal . . . .	Lead . . 80 Antimony . 20	The melted alloy expands at the moment of solidification.
Shot or Bullet metal .	Lead . . 98 Arsenic . 2	

*International Atomic Weights.*

O = 16.			O = 16.		
Aluminium . . .	Al	27·1	Neodymium . . .	Nd	144·3
Antimony . . .	Sb	120·2	Neon . . . . .	Ne	20·2
Argon . . . . .	A	39·88	Nickel . . . . .	Ni	58·68
Arsenic . . . . .	As	74·96	Niton (radium ema-		
Barium . . . . .	Ba	137·3	nation) . . . . .	Nt	222·4
Bismuth . . . . .	Bi	208·0	Nitrogen . . . . .	N	14·01
Boron . . . . .	B	11·0	Osmium . . . . .	Os	190·9
Bromine . . . . .	Br	79·92	Oxygen . . . . .	O	16·00
Cadmium . . . . .	Cd	112·40	Palladium . . . . .	Pd	106·7
Cæsium . . . . .	Cs	132·81	Phosphorus . . . . .	P	31·04
Calcium . . . . .	Ca	40·07	Platinum . . . . .	Pt	195·2
Carbon . . . . .	C	12·00	Potassium . . . . .	K	39·10
Cerium . . . . .	Ce	140·25	Praseodymium . . . . .	Pr	140·6
Chlorine . . . . .	Cl	35·46	Radium . . . . .	Ra	226·4
Chromium . . . . .	Cr	52·0	Rhodium . . . . .	Rh	102·9
Cobalt . . . . .	Co	58·97	Rubidium . . . . .	Rb	85·54
Columbium . . . . .	Cb	93·5	Ruthenium . . . . .	Ru	101·7
Copper . . . . .	Cu	63·57	Samarium . . . . .	Sa	150·4
Dysprosium . . . . .	Dy	162·5	Scandium . . . . .	Sc	44·1
Erbium . . . . .	Er	167·7	Selenium . . . . .	Se	79·2
Europium . . . . .	Eu	152·0	Silicon . . . . .	Si	28·3
Fluorine . . . . .	F	19·0	Silver . . . . .	Ag	107·88
Gadolinium . . . . .	Gd	157·3	Sodium . . . . .	Na	23·00
Gallium . . . . .	Ga	69·9	Strontium . . . . .	Sr	87·63
Germanium . . . . .	Ge	72·5	Sulphur . . . . .	S	32·07
Glucinum . . . . .	Gl	9·1	Tantalum . . . . .	Ta	181·5
Gold . . . . .	Au	197·2	Tellurium . . . . .	Te	127·5
Helium . . . . .	He	3·99	Terbium . . . . .	Tb	159·2
Holmium . . . . .	Ho	163·5	Thallium . . . . .	Tl	204·0
Hydrogen . . . . .	H	1·008	Thorium . . . . .	Th	232·4
Indium . . . . .	In	114·8	Thulium . . . . .	Tm	168·5
Iodine . . . . .	I	126·92	Tin . . . . .	Sn	119·0
Iridium . . . . .	Ir	193·1	Titanium . . . . .	Ti	48·1
Iron . . . . .	Fe	55·84	Tungsten . . . . .	W	184·0
Krypton . . . . .	Kr	82·92	Uranium . . . . .	U	238·5
Lanthanum . . . . .	La	139·0	Vanadium . . . . .	V	51·0
Lead . . . . .	Pb	207·10	Xenon . . . . .	Xe	130·2
Lithium . . . . .	Li	6·94	Ytterbium (Neoyt-		
Lutecium . . . . .	Lu	174·0	terbium) . . . . .	Yb	172·0
Magnesium . . . . .	Mg	24·32	Yttrium . . . . .	Yt	89·0
Manganese . . . . .	Mn	54·93	Zinc . . . . .	Zn	65·37
Mercury . . . . .	Hg	200·6	Zirconium . . . . .	Zr	90·6
Molybdenum . . . . .	Mo	96·0			

## APPENDIX

### WEIGHTS, MEASURES, ETC.

#### *Measures of Length.*

The English yard is the distance at 62° F. between two marks on a bronze bar deposited at the offices of the Board of Trade.<sup>1</sup>

The metre is the length at 0° C. of a platinum bar, preserved at Paris. It was intended to be one ten-millionth part of the earth's quadrant.

1 yard = 0'9144 m.	1 metre = 1'0936 yard.
1 foot = 0'3048 m.	„ = 3'2809 feet.
1 inch = 0'0254 m.	„ = 39'37 inches.
	1 centimetre = 0'3937 inch.
	<i>i.e.</i> nearly $\frac{2}{5}$ inch.
	1 kilometre = 0'6214 mile.
	<i>i.e.</i> nearly $\frac{5}{8}$ mile.

#### *Measures of Capacity.*

English—1 pint = 34'683 cub. inches = 568'23 c. cm.

1 gallon = 0'16 cub. foot = 4'546 litres.

Metric—1 litre = 1 cubic decimetre = 61'0363 cub. inches  
= 1'76 pint = 0'2201 gallon.

One gallon of water weighs 10 lbs.

One cubic foot of water at 39° F. weighs 62'415 lbs., *i.e.* nearly 1000 ozs.

#### *Measures of Mass.*

English—1 pound av. = 7000 grains = 453'593 grams.

1 ounce av. = 437'5 grains = 28'35 grains.

Metric—1 gram = mass of 1 c. cm. of water = 15'43 grains.

1 kilogram = 1000 grams = 2'2046 lbs.

<sup>1</sup> Copies of the English Standard Yard and other English measures may be seen on the steps on the north side of Trafalgar Square, London.

*Miscellaneous Data.*

Mass of 1 cub. foot of air	=	0.080728 lb.
Mass of 1 litre of air	=	1.2932 grams.
Normal atmospheric pressure	=	760 mm. of mercury
	=	29.922 inches of mercury.
A halfpenny is one inch in diameter and weighs		0.2 ounce.
Latent heat of water . . . . .		79.25
Latent heat of steam . . . . .		536

## QUESTIONS

1. What do you understand by the terms "Matter" and "Energy"?
2. What is meant by (a) "Force," (b) "Mechanical Work"?
3. Distinguish between a "physical" and a "chemical" change.
4. What is the effect of continued heating upon sulphur, ice, iodine, oxide of mercury, chalk? Which of these undergo chemical change when heated?
5. Give examples of chemical change, and show in each case how you would know that a chemical change had occurred.
6. What is double decomposition? What kinds of substances can take part in such a change, and under what conditions?
7. What are the chief points of difference between mixtures and compounds?
8. Classify the following as elements, compounds, and mixtures:—iron, brass, lime, blue vitriol, common salt, sugar, sulphur, mortar, air, charcoal, sulphide of iron, water, red-lead.
9. Distinguish between the terms "Mass" and "Weight."
10. Describe carefully what you observe when sulphur and iron filings are mixed together and heated.
11. Classify the following as physical and chemical changes:—The rusting of iron, the electrification of vulcanite, the slaking of lime, the melting of ice, the magnetisation of steel, decay, the burning of coal, the making of a photographic print, the drying of gum, the hardening of varnish, and the drying of paint.



12. How would you separate each of the following mixtures into its components?—

- (1) A mixture of sulphur and iron filings.
- (2) " " sand and salt.
- (3) " " charcoal and sugar.
- (4) " " iodine and charcoal.
- (5) " " sugar and salt.
- (6) Black gunpowder.

13. Mention some of the properties by virtue of which the following substances have commercial value:—Iron, copper, coal, petroleum, limestone, platinum, oxygen.

14. Explain how it is that a waterfall may have commercial value.

15. State Boyle's Law. How can it be proved experimentally?

16. What is a "Natural Law"? State the law which expresses the relation between the volume of a gas and the temperature at which it exists. Describe experimental proofs of this law.

17. What instrument is used for measuring temperature? Describe the construction of a usual form of this instrument.

18. What is a degree Centigrade? Compare the values of the Centigrade, Réaumur, and Fahrenheit degrees.

19. What is "Absolute Temperature"? Show that Charles' Law may be expressed in the form, "The volume of a gas is proportional to its absolute temperature."

20. How would you prepare and collect a few jars of oxygen? Describe experiments for demonstrating the properties of the gas.

21. What do you understand by the term "combustion"? What is a "supporter of combustion"?

22. In what respects does the rusting of iron differ from what takes place when iron is burned in oxygen?

23. What are the usual methods employed in the commercial preparation of oxygen?

24. How is oxygen obtained from potassium chlorate? By what means can the evolution of the gas be facilitated?

25. What happens when the following substances are strongly heated in contact with the air:—Copper, tin, iron, magnesium, potassium chlorate, gold, sulphur, phosphorus?

26. What is the relation of the oxygen in the air to respiration?

27. How could you obtain nitrogen from air? What are the chief properties of the gas? How can it be made to combine with (a) oxygen, (b) magnesium?

28. Compare the effects of burning the following in an enclosed volume of air:—Phosphorus, a candle, coal gas.

29. Describe an experiment which shows that the boiling point of a liquid is dependent upon the pressure.

30. Account for the fact that water is never found in nature in a pure state. Mention some of the more common impurities.

31. Describe the effect upon the volume of water by cooling it from  $15^{\circ}\text{C.}$  to  $-15^{\circ}\text{C.}$

32. What are the advantages of the use of hot water or steam for warming buildings?

33. Impurities in water may be either in suspension or in solution. Distinguish between these two conditions.

34. Describe a solubility curve. Construct one for ammonium chloride from the following figures.

Temperature in degrees Centigrade.	Mass in grams dissolved by 100 grams of water.	Temperature in degrees Centigrade.	Mass in grams dissolved by 100 grams of water.
$-15^{\circ}$	24.5 grams.	$50^{\circ}$	50.4 grams.
$0^{\circ}$	29.4 "	$60^{\circ}$	55.2 "
$5^{\circ}$	31.2 "	$70^{\circ}$	60.2 "
$15^{\circ}$	35.2 "	$80^{\circ}$	65.6 "
$20^{\circ}$	37.2 "	$90^{\circ}$	71.3 "
$30^{\circ}$	41.4 "	$100^{\circ}$	77.3 "
$40^{\circ}$	45.8 "	$110^{\circ}$	83.8 "

35. Compare the solubility of solids and gases in water, particularly as regards the influence of temperature and pressure upon the amount dissolved.

36. What is a crystal? How could you obtain (a) lead chloride, (b) common salt, in a crystalline form?

37. Explain the term "Water of crystallisation." Give examples of substances which contain it.

38. What information would you require before you permitted any particular water to be used for drinking purposes?

39. How would you carry out the electrolysis of water? Make a sketch of the necessary apparatus. What information does the electrolysis give you as to the composition of water?

40. By what methods is hydrogen obtainable from water? What is the action of metallic sodium upon water? Compare it with that of potassium and of calcium respectively.

41. How could hydrogen be obtained from sulphuric acid?

42. Describe experiments illustrating the chief properties of hydrogen.

43. Hydrogen is said to be a reducing agent. How would you demonstrate this by experiment?

44. Show how the reduction of copper oxide by hydrogen provides a means of determining the composition of water by weight.

45. How would you show that water is one of the products of combustion of a candle?

46. Why are the common names of familiar substances not in general use in chemistry?

47. Distinguish between a symbol, a formula, and an equation. Classify the following:—Ca, CaCl<sub>2</sub>, Cu, Co, CO, O, O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O. Why are the symbols Na and Fe respectively used for sodium and iron?

48. Why do we speak of the *laws* of definite and multiple proportions, and of the atomic *theory*?

49. What is the difference between the atomic and molecular weight of an element? Would it be wrong to apply either of these terms to compounds? if so, why?

50. Show that the "equivalent" of some elements is the same as the atomic weight, and in other cases it is only a fraction of the atomic weight. How do you account for this?

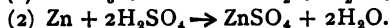
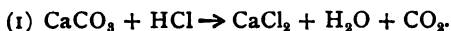
51. What do you understand by the term "percentage composition" of a substance? Show how to calculate from the formula (a) the percentage composition of a compound, (b) the amount by weight of each component in any other stated quantity.

52. What is the meaning of the signs, +, →, ⇌, used in writing equations?

53. Explain fully the meaning of the equation—



Correct the following equations :—



54. Compare the following formulæ and show what is the valency of each of the elements represented :—



55. Write down constitutional formulæ for each of the following :—Magnesium pyrophosphate, dichlor-ethane, ethylene-dichloride, ethylene, acetylene, hydrocyanic acid, grape sugar, soap, fat, benzene.

56. Distinguish between an acidic and a basic oxide.

57. What are the chief properties of (a) acids, (b) alkalis.

58. What are salts? Mention various ways in which they may be prepared.
59. Why are the acids often referred to as salts of hydrogen?
60. What is the action of (a) dilute sulphuric acid, (b) hydrochloric acid, upon the following metals:—Iron, zinc, magnesium, copper, aluminium? Write equations representing these reactions.
61. Give examples of a mono-basic, a di-basic, and a tri-basic acid, and write the formulæ of the normal salts which each forms with potassium, calcium, and aluminium.
62. How would you show that sulphuric acid is di-basic?
63. Normal sodium sulphate yields a neutral solution with water, while a solution of normal sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) is alkaline. How do you account for the difference?
64. What is the action of heat upon the following oxides:—Copper oxide ( $\text{CuO}$ ), lime, litharge, lead dioxide, manganese dioxide, barium peroxide, mercuric oxide, zinc oxide?
65. Compare the action of hydrochloric acid upon the peroxides of manganese and barium.
66. What can be observed when a solution of hydrogen peroxide is allowed to act upon (a) an acidulated solution of potassium iodide, and (b) a solution of potassium permanganate acidulated with sulphuric acid?
67. In what forms does calcium occur in nature?
68. Describe the industrial process known as lime-burning. Criticise the term.
69. What is a reversible reaction? Why is the action between lime and carbon dioxide considered reversible?
70. What is mortar? Discuss the changes which take place when it hardens.
71. What is gypsum? What changes take place in it when it is heated?
72. What is the cause of the "setting" of plaster of Paris?
73. What compounds are formed when carbon dioxide is passed for a long time into (a) caustic soda, (b) barium hydroxide, (c) lime-water?
74. What are the various causes of "hardness" in water?
75. What is boiler "fur" or "scale"? How is it produced, and in what way may its formation be prevented?
76. What are the chief processes used for softening water intended for drinking?
77. How is the liquefaction of gases generally carried out? What do you understand by the terms "critical temperature" and "critical pressure"?

78. How would you show that carbon dioxide contains carbon?

79. Why do we represent carbon dioxide by the formula  $\text{CO}_2$ , and carbon monoxide by the formula  $\text{CO}$ ?

80. Discuss the various causes of "stuffiness" in rooms.

81. What is a carbonate? What is the general action of acids upon carbonates? Give examples with equations.

82. Discuss the relation of carbon dioxide to plant and animal life.

83. Give an account of the natural occurrence, properties and uses of common salt.

84. How would you prepare and collect a few jars of dry hydrochloric acid gas?

85. Account for the name oxy-muriatic acid which was originally given to the gas now known as chlorine.

86. What is the effect of treating hydrochloric acid with oxidising agents? Write equations representing the interaction of the acid with manganese dioxide, potassium bichromate, potassium permanganate. What are the chief properties of the gas evolved?

87. Four jars of gas are given to you—

(a) contains carbon dioxide

(b) " nitrogen

(c) " hydrogen

(d) " chlorine.

By what tests could you identify the contents of each jar?

88. State Avogadro's hypothesis, and show how it enables us to compare the weights of the molecules of gases.

89. Why is hydrochloric acid gas represented by the formula  $\text{HCl}$ ?

90. What is *aqua regia*? Explain why its properties differ from those of either of the acids of which it is composed.

91. What methods are in use for the preparation of soda-crystals?

92. Write chemical formulæ for the following common substances:—Caustic soda, washing soda, common salt, limestone, quicklime, Glauber salt, Chili saltpetre, borax. What is the effect of heat upon these substances?

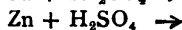
93. In what forms does sulphur occur in nature? How is it obtained in a pure state?

94. Sulphur is said to exhibit allotropy. Explain the term, and show how the various allotropic modifications of sulphur may be obtained.

95. What is the action of hydrochloric acid upon (a) iron, (b)

sulphur, (c) a mixture of iron and sulphur, (d) the substance formed when iron and sulphur are heated together?

96. Complete the following equations:—



What are the conditions under which the reactions represented by these equations most readily take place?

97. Give a short account of the method generally employed for preparing sulphuric acid on a commercial scale.

98. Comment upon the following names, all of which are applied to a solution of the same gas in water:—Sulphuretted hydrogen, hydrogen sulphide, hydrosulphuric acid.

99. What is ozone? How can it be prepared? How has its constitution been discovered?

100. Compare the properties of ozone with those of oxygen and hydrogen peroxide.

101. What difference, if any, would you expect to find in the composition of wood ashes, coal ashes, and bone ashes?

102. What are now the chief sources of potassium compounds? How can the metal itself be obtained from its chloride?

103. How would you obtain (a) potassium sulphate from potassium carbonate, and (b) potassium carbonate from potassium sulphate?

104. What are the chief points of difference between the properties of the yellow and red modifications of phosphorus?

105. Describe briefly the methods employed in the manufacture of phosphorus, and show what is the special function of each of the substances used.

106. What are the essential characteristics of sand and clay respectively? Upon what do these properties chiefly depend? What minerals are generally present in each?

107. What substances enter into the composition of ordinary glass?

108. What is the chemical composition of the substances commercially known as corundum, superphosphate, fluorspar, carborundum, borax? For what purposes are these substances used?

109. Discuss the use of preservatives in food

110. What are the chemical actions involved in the various

processes of bleaching? What substances are usually employed for this purpose?

111. How would you detect boracic acid in butter?

112. When glass is brought into contact with hydrofluoric acid, it is corroded. What chemical actions take place, and what substances are formed?

113. Distinguish between colloid and crystalline substances. How can they be separated from each other when in solution?

114. What is meant by destructive distillation? Classify the principal products obtained by destructive distillation of wood and coal respectively.

115. What is water-gas? How is it made and for what is it used?

116. What are the experimental reasons for representing ammonia by the formula  $\text{NH}_3$ .

117. The compound  $\text{NH}_4\text{OH}$  (ammonium hydroxide) has never been isolated, but it is believed that it exists in aqueous solutions of ammonia gas. Upon what experimental evidence is this belief based?

118. What are the more important chemical properties of nitric acid? How are the lower oxides of nitrogen obtained from it?

119. How is nitric acid prepared? What are the chief commercial sources of the acid?

120. State precisely what would be observed when the following substances are heated strongly:—Ammonium nitrate, ammonium chloride, potassium nitrate, lead nitrate, ammonium carbonate, silver nitrate. Express the reactions which take place by means of equations.

121. What do you understand by the term "organic matter"? What are the elements most frequently present in organic matter?

122. What is the object of filtering water through charcoal? How far is this object effected?

123. In what way do the following substances differ from one another:—Peat, lignite, house coal, anthracite?

124. Name some of the most important by-products of the preparation and purification of coal-gas. For what purposes are they employed?

125. What are the chief properties of the gas prepared by the action of concentrated sulphuric acid upon potassium ferrocyanide? By what other methods can the gas be obtained?

126. What is sal-ammoniac? From what did it receive its name? What happens when it is heated with chalk?

127. What is an ammonium salt?

128. What methods are now employed for obtaining the nitrogen of the atmosphere in a form in which it can be used as plant food?

129. Compare the forms in which plants and animals require nitrogenous food.

130. What is the nature of the change which takes place when certain carbohydrates are boiled for some time with dilute acid? What substances are formed when cane sugar, starch, milk sugar, and cellulose respectively are treated in this way?

131. What is an enzyme? Give a short account of some of the changes brought about by their action.

132. What substances are formed when (a) cane sugar, (b) metallic copper are treated with concentrated nitric acid? Mention the chief properties of the solid products.

133. How would you show the presence of nitrogen in an organic compound? Upon what chemical actions is your method based?

134. What is the action of heat upon the following:—Cream of tartar, mercuric cyanide, ammonium cyanate?

135. By what tests would you recognise cane sugar, glucose, and starch?

136. What connection can be traced between marsh gas, paraffin oil, and vaseline? Mention any other commercial products of similar nature.

137. What is a homologous series? Mention homologous series the members of which contain (a) oxygen, (b) chlorine, (c) nitrogen, (d) none of these elements. Give the names and formulæ of substances which are typical members of each of the series you have referred to.

138. Why is common alcohol represented by the formula  $C_2H_5OH$ ? By what other names is the substance known? How is it obtained commercially? Give the names and formulæ for any six other alcohols, and show how these formulæ represent their common properties and their differences.

139. Describe briefly the more important properties of aldehydes. What relation do these compounds bear (a) to alcohol, (b) to acids? How would you experimentally demonstrate this relation?

140. Distinguish between an ether and an ester. Describe the method of preparation of one of each of these compounds.

141. What two substances can be represented by the empirical formula  $C_2H_2O$ ? How would you distinguish one of these compounds from the other?



142. What is an olefine? Why are the olefines regarded as unsaturated? How is this condition indicated in their chemical formulæ? Write the general formula for the group.

143. Show by means of a sketch the structure of an ordinary candle flame. Why do the flames of burning alcohol, hydrogen, and a Bunsen burner give out little or no light?

144. What is the difference between a tertiary alcohol and a tri-hydric alcohol? Give examples of each.

145. What is the difference between glycol and glyocol? What products are obtained by the oxidation of each?

146. How is soap made? Give equations. What are the characteristics of potash soaps, soda soaps, stearin soaps, olein soaps, calcium soaps, ammonia soaps, lead soaps? What is the composition of ordinary household soap?

147. Distinguish between a "carbohydrate" and a hydrocarbon.

148. Glucose and fructose are both represented by the empirical formula  $C_6H_{12}O_6$ , yet they have different properties. What are these differences, how are they accounted for?

149. What is milk sugar? How could you distinguish, in the laboratory, between cane sugar and milk sugar?

150. Explain the term "hydrolysis." By what agencies are hydrolytic changes brought about?

151. What do you understand by fermentation? Mention four different types of fermentation and give the name of the chief product in each case.

152. What are the respective actions of yeast and baking powder in dough? Ammonium carbonate is sometimes used as baking powder; what is its action?

153. What is an amine? How does it differ from an amide?

154. What are "formalin" and formamide respectively?

155. What is the chief nitrogenous compound excreted by animals? Give two distinct methods by which it may be artificially prepared.

156. What do you know of the following naturally occurring compounds:—Amygdalin, salicin, citric acid, malic acid, starch, asparagin?

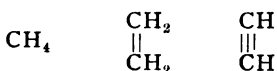
157. What do you understand by the terms, "isomerism," "polymerism"? Give examples.

158. What is meant by the "flash point" of a lamp oil? What is the legal flash point in Great Britain?

159. Mention various substances which are in common use as lubricants. What are the essential properties of lubricants?

160. What is a fuel? Compare light petroleum and alcohol as fuels.

161. The compounds, marsh gas, ethylene, and acetylene are respectively represented by the formulæ—



What are the experimental data for these formulæ?

162. Distinguish between a "wax" and a "fat." What is paraffin wax?

163. By what tests would you distinguish between a mineral oil, and one of animal or vegetable origin?

164. Contrast the action of concentrated sulphuric acid upon a paraffin hydrocarbon and upon benzene.

165. Write a short account of the substances which can be formed by the action of sulphuric acid upon alcohol. What are the conditions most favourable to the formation of each?

166. In what respects do the alcohols resemble the hydroxides of metals?

167. Account for the cleansing effect of soap. What is the action of the various kinds of hard water upon soap?

168. What is calcium cyanamide? Why can this substance be used as a nitrogenous manure?

169. What is coal tar? Account for its commercial importance.

170. What is benzene? How does it differ from the liquid often sold as benzine?

171. How is phenol prepared? What are its chief properties and uses?

172. How can aniline be prepared from benzene? Compare its properties with those of ammonia.

173. Write formulæ for the substances commercially known as (1) oil of mirbane, (2) oil of bitter almonds, (3) carbolic acid, (4) oil of winter green.

174. Criticise the name "carbolic acid" as applied to phenol. Distinguish between a phenol and an alcohol.

175. What is a "metal"? Classify the following as metals and non-metals:—Silver, arsenic, phosphorus, potassium, gold, aluminium, sulphur, hydrogen, silicon, magnesium. Give reasons for your classification.

176. What is dolomite? How would you prepare from it some crystallised magnesium sulphate?

177. Discuss the suitability of aluminium for cooking utensils.

178. What use is made of aluminium compounds in dyeing? What other compounds are used for a similar purpose?

179. What are the chemical actions involved in iron smelting?

180. Distinguish between wrought iron, cast iron, and steel.

181. What is basic slag? For what purposes is it used?

182. What happens when steam is passed over red-hot iron, and when hydrogen is passed over red-hot iron oxide? Explain why these reactions take place.

183. When lead oxide is warmed with a slight excess of dilute nitric acid it dissolves. What is produced, and how can it be obtained in crystals? What would you observe if these crystals were heated in a hard glass tube? Give equations representing the changes.

184. The names "Vitriol of Mars," green vitriol, copperas, sulphate of the protoxide of iron, ferrous sulphate, have all been in use at some time or other for the same compound. Show how they indicate the progress of chemical knowledge.

185. Distinguish between a ferrous and a ferric salt. How can a ferrous be converted into a ferric salt, and a ferric into a ferrous salt?

186. The following commercial materials are all iron compounds. Write their formulæ, describe them, and mention their chief uses. Green vitriol, Prussian blue, Venetian red, jeweller's rouge.

187. What are the most familiar compounds of manganese? In what ways do they find industrial application?

188. Iron is often covered with a protective coating of zinc, nickel, or tin. How are these coatings put on the iron?

189. What substances are used to impart a violet, blue, yellow, green, or red colour to glass or porcelain?

190. What is the "passive state"? How can iron and chromium be made to assume this state?

191. A dilute solution of cobalt chloride has been used as a writing ink, the words becoming visible only on warming. What property of the salt is thus made use of? Mention any parallel cases.

192. From what property has the metal chromium received its name? Illustrate your answer by reference to the compounds of chromium.

193. What are the chief compounds used as white and yellow pigments? What are the advantages and disadvantages attending the use of each of them?

194. Write the chemical formulæ for the following common

ores :—Zinc blende, iron pyrites, galena, malachite, cuprite, copper pyrites, pyrolusite, bauxite, cassiterite, haematite.

195. If you were given some black copper oxide, how would you obtain from it some crystallised copper nitrate?

196. Compare the action of a solution of caustic soda with that of ammonia solution, upon a solution of copper sulphate.

197. State carefully what changes take place when the following chain of reactions is carried out. Give equations.

(1) Copper is dissolved in concentrated nitric acid.

(2) The solution is evaporated with concentrated sulphuric acid.

(3) The residue is dissolved in water.

(4) Zinc turnings are placed in the solution.

198. How would you prepare (1) cuprous oxide, (2) cuprous chloride, (3) cuprous iodide from cupric sulphate?

199. What is verdigris? Account for the green colour assumed by a copper roof which has been exposed for a long time to the weather.

200. What are the advantages and disadvantages attending the use of copper for cooking utensils?

201. What dangers attend the use of lead pipes for the supply of drinking water? With what kinds of natural waters is the danger greatest? Why?

202. Compare the properties of the oxides of lead which are represented by the formulæ  $PbO$ ,  $Pb_2O_3$ ,  $PbO_2$ .

203. Describe the substances known as corrosive sublimate and calomel. How could you obtain the latter from the former compound?

204. Account for the blackening of silver which has come in contact with white of egg or with vulcanised indiarubber.

205. What property of silver salts enables them to be used in photography?

206. What are the chief uses of gold other than for jewellery and coinage?

207. What is the action of *aqua regia* upon gold and platinum? What is the effect of heat upon the compounds formed?

208. What are solders? For what purposes are they used?

209. How can the two chlorides of tin be prepared?

210. Why is arsenic generally considered a non-metal? Compare its properties with those of antimony and phosphorus.

211. How can small quantities of arsenic be detected?

212. Classify the following as acidic and basic oxides. What

is the action of hydrochloric acid and of nitric acid and caustic soda upon each. Chromium trioxide  $\text{CrO}_3$ , arsenious oxide  $\text{As}_2\text{O}_3$ , cuprous oxide  $\text{Cu}_2\text{O}$ , zinc oxide  $\text{ZnO}$ , alumina  $\text{Al}_2\text{O}_3$ , litharge  $\text{PbO}$ , chromic oxide  $\text{Cr}_2\text{O}_3$ , tin dioxide  $\text{SnO}_2$ .

### EXAMPLES FOR CALCULATION

1. Calculate the equivalent of magnesium if 10 grams of the metal combine with oxygen to form 16.67 grams of the oxide.

2. If 1.5 grams of zinc are dissolved in acid, and 511 c.c. of hydrogen at N.T.P. are liberated, what is the equivalent of zinc?

3. Calculate the percentage composition of (1) potassium permanganate  $\text{KMnO}_4$ , (2) cane sugar  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ , (3) ferrous sulphate  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , (4) sodium chlorate  $\text{NaClO}_3$ .

4. Calculate the formulæ of the four compounds whose percentage compositions obtained by analysis are as follows:—

(1) Carbon	58.54	(2) Sodium	14.29
Hydrogen	4.07	Sulphur	9.94
Nitrogen	11.38	Oxygen	19.87
Oxygen	26.01	Water	55.90
(3) Potassium	30.71	(4) Potassium	42.39
Sulphur	25.19	Iron	15.22
Oxygen	44.09	Carbon	19.56
		Nitrogen	22.82

5. A volume of 500 cubic centimetres of air measured at N.T.P. has its pressure increased to 780 mm., and its temperature raised to  $15^\circ\text{C}$ . What volume will it now occupy?

6. A volume of 350 c.c. of gas measured at N.T.P. has its pressure raised to 790 mm. To what must the temperature be increased that the volume may remain unaltered?

7. A volume of gas is measured at 770 mm. and  $15^\circ\text{C}$ . The pressure is increased, and by raising the temperature to  $63^\circ\text{C}$ . the volume is kept constant. What has been the increase in pressure?

8. A volume of gas measured at normal pressure and  $15^\circ\text{C}$ . has its temperature raised to  $50^\circ\text{C}$ . To what pressure must the gas be subjected that its volume may be one-half of the original volume?

9. What volume of chlorine would be obtained if 10 grams of

manganese dioxide were treated with hydrochloric acid? The gas is to be measured at N.T.P.

10. If 25 grams of calcium carbonate were treated with hydrochloric acid, and the resulting gas passed into an excess of caustic soda solution, what would be the increase in weight of this solution?

11. Five grams of a mixture of calcium carbonate and an inactive substance were treated with hydrochloric acid and found to lose 1.2 grams in weight. Calculate the percentage of calcium carbonate in the mixture.

12. What weight of quicklime is obtainable from 150 grams of pure calcium carbonate?

13. If 5 grams of caustic potash, KOH, be neutralised with sulphuric acid, what weight of potassium sulphate would be obtained?

14. What weight of copper oxide, CuO, would be required to combine with 200 grams of a solution of sulphuric acid containing 49 per cent. of pure acid ( $H_2SO_4$ )? What weight of crystallised copper sulphate would be formed?

15. If 3 litres of a mixture of oxygen and ozone (measured at a temperature of  $15^\circ C.$ ), containing 5 per cent. of the latter, be heated to  $250^\circ C.$ , what will be the volume of the gas at this latter temperature, pressure remaining constant?

16. What volume of sulphuretted hydrogen at N.T.P. could be obtained by the action upon ferrous sulphide of 15 grams of a solution of hydrochloric acid containing 40 per cent. of the gas (HCl)? What weight of sulphide would be required?

17. What weight of nitrate of soda contains the same quantity of nitrogen as, one hundredweight of sulphate of ammonia, (a) when both substances are pure, (b) when the former contains 8 per cent. of common salt and the latter 3 per cent. of moisture?

18. What weight of bone ash, assumed to be pure calcium phosphate, would be required for the formation of one hundredweight of super-phosphate? What weight of this latter material will contain 100 lbs. of phosphorus pentoxide?

19. A sample of soil—of which one acre, 9 inches deep, weighed  $2\frac{1}{2}$  million pounds—was found to contain 0.01 per cent. of phosphorus pentoxide; what quantity of phosphate of lime (tricalcic orthophosphate) per acre is this equivalent to?

20. What volume of gas measured at  $150^\circ C.$ , and 760 mm. pressure, would be obtained by heating 10 grams of ammonium nitrate?

21. If limestone containing 90 per cent. of calcium carbonate cost, say, five shillings per ton at the quarry, and the cost of carriage,

burning, etc., amounted to, say, ninepence per ton of limestone, at what price per ton could the quicklime be sold at the kiln, so as to cover expenses?

22. What weight of caustic potash would be required to make one ton of soft soap, assuming that it was made from palm oil, and that this was pure palmitin?

23. Potatoes contain, say, 18 per cent. of starch. What weight of glucose could be obtained from three hundredweight of such potatoes?

24. Five grams of cheese are so treated that all its nitrogen is converted into ammonia. If it is found that from the ammonia so liberated 1.06 grams of ammonium sulphate can be formed, calculate the percentage of nitrogen in the cheese.

25. What weight of common salt is required to provide sufficient chlorine to liberate all the iodine in 100 grams of a 10 per cent. solution of potassium iodide?

26. Fifty cubic centimetres of a solution of hydrogen peroxide were found to liberate 0.3 grams of iodine from potassium iodide in the presence of acid. Calculate the percentage of hydrogen peroxide in its solution.

27. What weight of soda crystals can be theoretically obtained from one pound of common salt?

28. What weight of wrought iron containing 0.8 per cent. of carbon is theoretically obtainable from 255 tons of hæmatite free from impurities?

29. What relative quantities of cerussite ( $\text{PbCO}_3$ ) and galena would yield equal weights of red lead?

30. Calculate the weight of the residue left when concentrated nitric acid acts upon 5 grams of a solder containing 40 per cent. of lead and 60 per cent. of tin.

31. What would be the weight of the solid thrown down when 5 grams of zinc were allowed to act upon excess of a solution of copper sulphate?

32. A certain monobasic acid forms a silver salt containing 63.53 per cent. of silver. What is the molecular weight of the acid.

33. Find the number of grams of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) in a litre of a solution of the acid, 40 cubic centimetres of which neutralise 2.92 grams of pure sodium carbonate. What volume of hydrogen at N.T.P. would be liberated from 100 c.c. of the acid by the action of zinc?

34. What weight of calcium carbonate must be decomposed to yield sufficient carbon dioxide to convert 40 grams of sodium hydroxide into sodium bi-carbonate?

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## ANSWERS

1. 11'99.
2. 32'65.
3. (1) K 24'68. (2) C 42'11. (3) Fe 20'14. (4) Na 21'59  
Mn 34'81. H 6'43. S 11'51. Cl 33'34.  
O 40'50. O 51'45. O 23'02. O 45'07.  
H<sub>2</sub>O 45'33.
4. (1) C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, Nitro-benzene.  
(2) Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, Glauber salt.  
(3) K<sub>2</sub>S<sub>2</sub>O<sub>7</sub>, Potassium pyrosulphate.  
(4) K<sub>4</sub>FeC<sub>6</sub>N<sub>6</sub>, Prussian blue.
5. 513'947 c.c.
6. 10'8° C.
7. 128'1 mm. increase.
8. 1705 mm., i.e. 2'24 atmospheres.
9. 2'559 litres.
10. 11 grams.
11. 54'54 per cent.
12. 84 grams.
13. 7'768 grams.
14. CuO 79'5 grams, CuSO<sub>4</sub>·5H<sub>2</sub>O 249'4 grams.
15. 5'89 litres.
16. 1'83 litres H<sub>2</sub>S, 7'225 grams FeS.
17. (a) 144'2 lbs.; (b) 152'1 lbs.
18. (a) 68'61 lbs.; (b) 356'6 lbs.
19. 545'8 lbs.
20. 13'01 litres, of which one-third is nitrous oxide, and two-thirds water vapour.
21. 11s. 4'6d. per ton.
22. 426'72 lbs.
23. 67'2 lbs.
24. 4'498 per cent.
25. 3'526 grams.
26. 9'0598 per cent.
27. 2'448 lbs.
28. 179'956 tons.
29. 267 : 239 by weight.
30. SnO<sub>2</sub> 3'8 grams.
31. 4'879 grams Cu.
32. 62'8.
33. 67'49 grams; 13'842 litres.
34. 100 grams.

**THE END**





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